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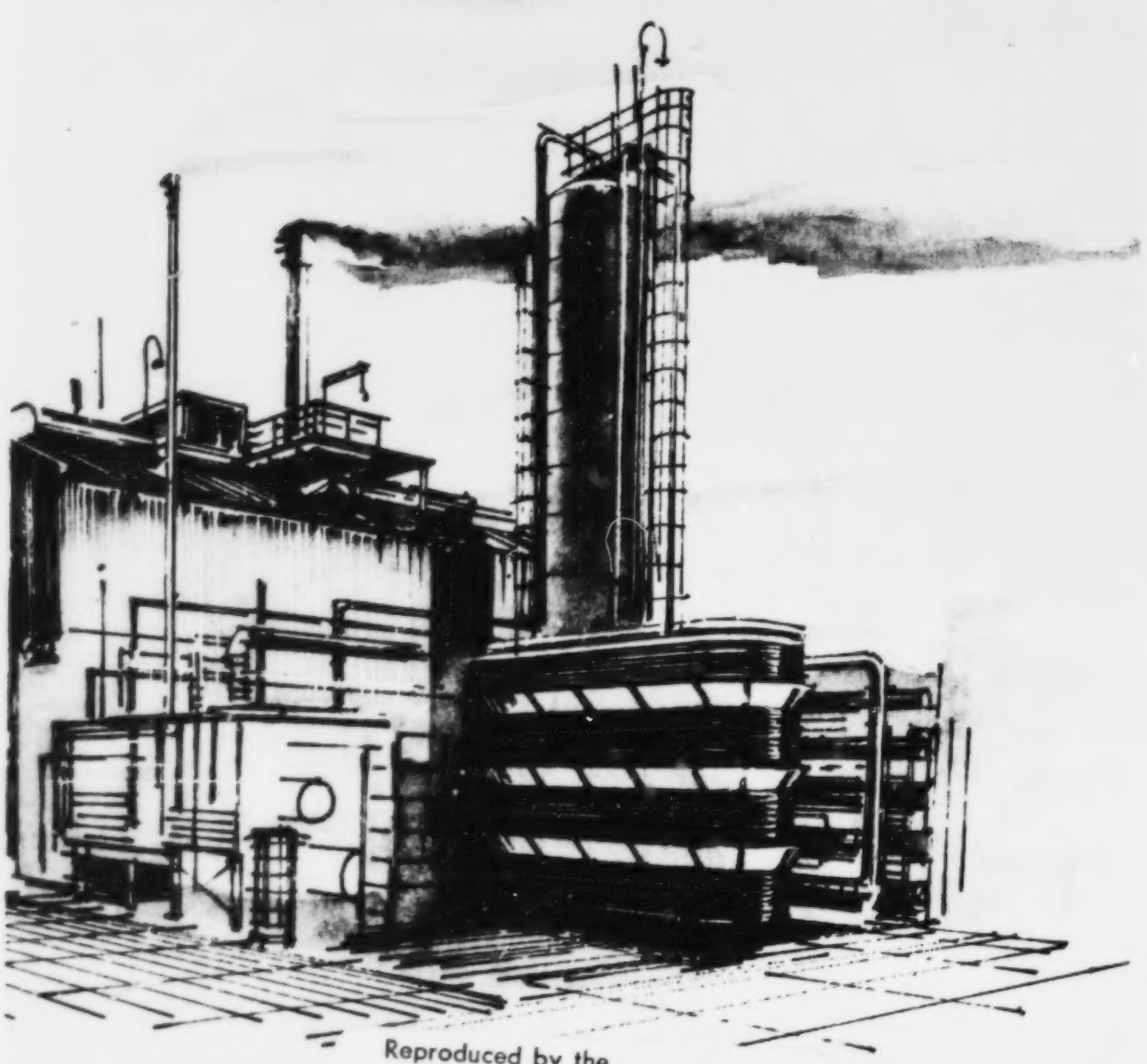
Air Pollution

# ATMOSPHERIC EMISSIONS FROM NITRIC ACID MANUFACTURING PROCESSES



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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

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# ATMOSPHERIC EMISSIONS FROM NITRIC ACID MANUFACTURING PROCESSES

**Cooperative Study Project**
**Manufacturing Chemists' Association, Inc.**
**and**
**Public Health Service**

**U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE**

Public Health Service
National Center for Air Pollution Control
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**Public Health Service Publication No. 999-AP-27**

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## PREFACE

To provide reliable information on the nature and quantity of emissions to the atmosphere from chemical manufacturing, the Manufacturing Chemists' Association, Inc. and the Division of Air Pollution, United States Public Health Service, Department of Health, Education, and Welfare entered into an agreement on October 29, 1962. A cooperative program was established to study emissions from selected chemical manufacturing processes and to publish information about them in a form helpful to air pollution control and planning agencies and to chemical industry management.* Direction of these studies is vested in an MCA-USPHS Steering Committee, presently composed as follows:

| Representing USPHS | Representing MCA |
|---|---|
| Austin N. Heller† | Willard F. Bixby† |
| John H. Ludwig | Louis W. Roznoy |
| Stanley T. Cuffe | Clifton R. Walbridge |
| Robert Porter | Elmer P. Wheeler |

Information to be published will describe the range of emissions during normal operating conditions and the performance of established methods and devices employed to limit and control these emissions. Interpretation of emission values in terms of ground-level concentrations and assessment of potential effects produced by the emissions are both outside the scope of this program.

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*The initial report in this series is *Atmospheric Emissions from Sulfuric Acid Manufacturing Processes*, PHS Publ. No. 999-AP-13, U. S. Government Printing Office, Washington, D. C., 60 cents.

†Principal representatives

## ACKNOWLEDGEMENTS

Many companies and individuals in the nitric acid industry have been helpful in carrying forward this study, and for their contributions the project sponsors extend their sincere gratitude.

Special thanks are due the following organizations for their participation in a program of stack sampling and analysis specifically for this study:

E. I. du Pont de Nemours and Company

Hawkeye Chemical Company

The Tennessee Valley Authority

Several companies also have provid[illegible] from their records additional stack sampling and analytical data, wh[illegible]h have been incorporated into this report.

Richard W. Gerstle of the Public Health Service and Ralph F. Peterson of E. I. du Pont de Nemours and Company were the investigators in the study and are the principal authors of this report. The sponsors acknowledge the contribution of E. I. du Pont de Nemours and Company in providing the services of Mr. Peterson.

## USE OF THIS REPORT

This report, one in a series concerning the atmospheric emissions from chemical manufacturing processes, has been prepared to provide information on nitric acid manufacture.

Background information is included to define the importance of the nitric acid industry in the United States. Basic characteristics of the industry are discussed, including growth rate in recent years, manufacturing processes, uses for the product, and the number of producing establishments, i.e., manufacturing sites, in existence at the present time.

A description is given for the ammonia oxidation process—the principal process in commercial use today—including the pressure variations used for reaction and absorption. Process information includes discussions of the normal operating variables that affect the types and quantities of emissions, the normal range of emissions, and methods of controlling emissions. Supplemental material provides detailed descriptions of sampling and analytical methods.

The emission data represent results from approximately 30 percent of the present number of establishments.* Most of these data have been gathered from production records of nitric acid producers. Data also include results from several stack-sampling programs conducted jointly during 1964 by the Manufacturing Chemists' Association and the United States Public Health Service. Results obtained are consistent with the values of the emissions otherwise reported.

The production of nitric acid has been a basic industry in the United States for at least 40 years, and the manufacturing procedures have become well established.

Emissions to the atmosphere from a nitric acid plant depend upon a number of factors, such as plant design, skill of operation, efficiency of absorption, and the use of special devices to reduce emissions. This report should be reviewed from time to time to determine whether revision is needed to reflect prevailing conditions.

Although this report has been prepared as a technical review for those concerned with the control of air pollution, it is expected that this information will also be helpful to chemical plant management and technical staffs. It may also be useful to engineering students, medical personnel, and other professional people interested in the atmospheric emissions from nitric acid manufacturing plants.

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*Establishment: A works having one or more nitric acid plants or units, each being a complete production entity.

# SUMMARY

## MANUFACTURING PROCESSES

Since 1930 most of the nitric acid made commercially in the United States has been produced by the ammonia oxidation process. Although various types of plants have been constructed for carrying out this synthesis, the basic chemistry is the same in all plants. It involves high-temperature oxidation of ammonia with air over a platinum catalyst to form nitric oxide, followed by oxidation of the nitric oxide to nitrogen dioxide and absorption in water to produce an aqueous solution of nitric acid. The nitrogen that enters the system in the air supplied to the process and small amounts of unreacted oxygen and nitrogen oxides, mainly NO and $NO_2$, are discharged from the absorber to the atmosphere. This discharge represents the main source of atmospheric emissions from nitric acid plants today. The composition of this exit gas, particularly its nitrogen oxides content, depends on the type of process employed and on the operating conditions.

## NITRIC ACID PRODUCTION

Production of nitric acid has increased sharply in the last 5 years. Since 1958, production has increased 70 percent to an annual rate of 4,609,000 tons in 1964.(*1*) This growth rate of about 9 percent per year may continue for several more years.

There are presently 74 nitric acid establishments having production capacities ranging from 500 to 380,000 tons per year (100 percent $HNO_3$ basis). Product acid varies in strength from 50 to 65 percent; most of it is in the range of 55 to 60 percent. The largest single use of the product is in the manufacture of fertilizer-grade ammonium nitrate.

## EMISSIONS FROM NITRIC ACID PROCESSES

### Nitric Acid Manufacture

The major source of atmospheric emissions is the absorption column in which nitrogen oxides are reacted with water to form nitric acid. The exit gas from the column contains unreacted nitrogen oxides (largely in the form of nitric oxide and nitrogen dioxide), oxygen, and nitrogen. Trace amounts of acid mist or vapor may also be present. Nitric oxide is a colorless gas; nitrogen dioxide is characterized by a reddish-brown color. The total concentration of nitrogen oxides normally ranges from 0.1 to 0.6 percent by volume of effluent prior to any treatment for control. Nitrogen dioxide accounts for about one half of the total nitrogen oxides. Emission data are shown in Tables 2, 3 and 4, (Pages 22, 24, and 25).

### Other Processes

Emissions of nitrogen oxides occur also with certain chemical operations where nitric acid is employed, as in nitration and oxidation. Small amounts of nitrogen dioxide are also lost from acid concentrators and acid storage tanks. These emissions are evidenced by their dense reddish-brown color, but generally their volume is small.

## CONTROL OF EMISSIONS

Factors that can cause heavy emissions of nitrogen oxides are (1) operation above design capacity, (2) production of acid stronger than that for which the plant was designed, (3) insufficient supply of oxygen to the system, and (4) leaks from heat exchangers. High cooling-water temperatures and atmospheric temperatures likewise reduce absorption efficiency and increase emissions; for this reason emissions are usually more noticeable in summer than in winter.

Emissions can be substantially reduced by installation of facilities to remove nitrogen oxides from the tail gas. Alkaline scrubbing systems or catalytic reduction equipment, presently used for this purpose, can reduce nitrogen oxides emissions by as much as 90 percent.

Scrubbing with caustic solutions may involve a problem of liquid waste disposal. Catalytic fume-abatement equipment is being used increasingly to reduce nitrogen oxides emissions. Plants equipped with catalytic fume eliminators usually operate with no visible plume. The heat generated in these eliminators is recovered in heat exchangers and a waste heat boiler, and also as power in recovery compressors or turbines. Catalytic fume elimination equipment is now found on about 15 percent of nitric acid plants. Capital costs range from $1.00 to $2.00 per scfm of tail gas, excluding such auxiliary equipment as waste heat boilers and controls.

### Emission Guidelines

Atmospheric emissions from nitric acid plants depend on plant operating conditions, production rates, and the use of control devices. As shown in Table 2, plants operating within design capacities and producing 55 to 60 percent nitric acid can limit nitrogen oxides concentration to 0.3 percent in the effluent stream leaving the nitric acid absorption column. On this basis a plant producing 300 tons per day will emit approximately 600 pounds of nitrogen oxides per hour, as shown in Figure 6. Installation of scrubbers or catalytic reduction equipment in the effluent gas stream can further reduce these emissions by 50 to 90 percent when the equipment is operating properly. Only trace amounts of nitric acid mist are normally emitted from a properly operated plant.

Emissions from nitric acid concentrators amount to about 10 pounds of nitrogen oxides per 1000 pounds of strong acid produced. Emissions during startup or shutdown procedures are usually lower than those that occur during normal operations.

# GROWTH OF NITRIC ACID INDUSTRY

## HISTORICAL BACKGROUND

The need for combined or "fixed" nitrogen in the growth and maintenance of all animal and plant life is well established and has been known since 1862. Nitrogen is "fixed" by various types of bacteria and is thus returned to the soil via the plant host upon which the bacteria may live. In addition, bacterial action on dead organic matter produces fixed nitrogen compounds. These amounts of fixed nitrogen compounds are not sufficient for today's large agricultural needs, nor are these nitrates available for making dyestuffs, explosives, nitrocellulose, and other products. Because of the insufficient supplies of naturally occurring fixed nitrogen, much attention has been given to the conversion of atmospheric nitrogen to various useful compounds, especially nitric acid.

Until the early 1900's, fixed nitrogen was obtained largely from Chilean saltpeter (sodium nitrate) or as a byproduct in coke manufacturing as ammonium sulfate. The Chilean saltpeter was used directly as a nitrate salt or converted to nitric acid by distilling with sulfuric acid. In the reaction between sulfuric acid and saltpeter, cast iron retorts were charged with 1,500 to 5,000 pounds of sodium nitrate; sulfuric acid was added, and the mixture was gently heated. The resulting nitric acid vapor was then condensed and withdrawn. Sodium bisulfate (niter cake) remaining in the retort could be sold occasionally as a byproduct.

The desire of manufacturers to reduce dependence on Chilean saltpeter around the time of the First World War stimulated developments of other methods of nitric acid production. The Haber process for ammonia production had also been introduced by 1910, and the combination of these two factors gradually caused a shift toward the newer and more economical ammonia oxidation method for manufacturing nitric acid.

Modern methods of nitric acid production involve oxidation of ammonia in air over a platinum catalyst followed by cooling of the resulting nitrogen oxides and their absorption in water. Use of this basic method dates back to about 1904, when Ostwald designed and built a small pilot plant for this process.(*2*) This plant initially used relatively large amounts of catalyst; however, developments in the use of preheated air and of electrically heated gauze-type catalyst helped conserve the expensive platinum.

Nitrogen oxides were also made by passing air through an electric arc. The intense heat caused about 2 percent of the nitrogen in the air to react with oxygen to form nitric oxide. The emerging gases were cooled rapidly to prevent decomposition and were oxidized to nitrogen dioxide and absorbed in water to make nitric acid. This process required large amounts of electric power and is presently not an economical method for nitric acid manufacture in this country.

Work in the United States on the production of nitric acid by ammonia oxidation was underway by 1916. Ammonia was obtained from calcium cyanamide, $CaCN_2$, and oxidized with air by passage through an electrically heated platinum gauze. In 1918 the Air Nitrates Corporation, acting as

agent for the United States Government, built a large plant for the production of nitric acid at Muscle Shoals, Alabama. This early plant was constructed entirely of acid-resistant brick and operated at atmospheric pressure. The slow absorption rates of the nitrogen dioxide in water at atmospheric pressure necessitated a large absorption volume, comprising 24 towers, each 1,220 feet square by 60 feet high, to produce 280 tons per day of acid. Because of the high initial building costs and the low strength of acid produced, the brick type of plant has become extinct. A number of atmospheric pressure plants were later constructed of stainless steel, and some of these are still in operation.

With the further development of acid-resistant metal alloys in the mid-1920's, nitric acid manufacturing techniques shifted toward the use of higher pressures. Operation at high pressures enabled the manufacturer to build a much smaller plant for the same acid production because nitrogen dioxide is absorbed much faster by water at high pressures. In the early plants, the high-pressure (80-psig) tail gas leaving the absorption system was simply vented to the atmosphere. By the mid-1930's, process efficiency had been significantly improved by reheating the 80-psig tail gas to about 500°F in a heat exchange system and using it to drive a reciprocating expander. The energy contained in the hot tail gas thus provided 30 to 40 percent of the power used for process air compression.

A further development in power recovery technology occurred about 1950, when gas expander turbines were adapted for this purpose. Gas turbines do not have the lubrication problems inherent in reciprocating expanders and therefore can operate at much higher temperatures. Recovery gas turbines may provide up to 90 percent of a plant's power requirements. Almost all nitric acid in the United States is now manufactured by a process in which the absorption portion, if not all of the process, operates at pressures ranging from 50 to 120 psig.

## CURRENT PRODUCTION AND USES

Table 1 shows the growth of nitric acid production over the past 25 years. The nitric acid industry is closely tied to the fertilizer industry; 75 percent of the nitric acid production goes into the manufacture of ammonium nitrate, much of which is used as fertilizer. A significant quantity of ammonium nitrate is used in commercial explosives. Substantial quantities of nitric acid are also used for nitrating organic compounds and for certain rocket fuels.

In January 1966, 74 establishments were producing nitric acid in the United States. Missouri and Kansas were the leading states in the production of nitric acid, with a combined capacity greater than 1 million tons of nitric acid per year. The largest concentration of nitric acid plants is in the midwestern and southeastern portions of the United States.

## FUTURE TRENDS

The ammonia oxidation process for nitric acid manufacture seems firmly entrenched as the most economical commercial process. The cost of ammonia

has shown a marked downward trend as a result of improved process technology, and therefore the cost of nitric acid has likewise decreased. In recent years much progress has been made in improving the efficiency of nitric acid plants, particularly in power utilization through recovery of energy from waste tail gas. The present trend is toward the building of larger plants with capacities of 500 or more tons of nitric acid (100 percent basis) per day. The proposed construction of an 800-ton-per-day unit was announced in October, 1965.

TABLE 1. GROWTH OF NITRIC ACID INDUSTRY IN UNITED STATES(*1*)

| Year | Production, Thousands of short tons 100% acid basis | Increase, % |
|---|---|---|
| 1939 | 168 | |
| 1947 | 1,189 | 608 |
| 1950 | 1,336 | 12.4 |
| 1955 | 2,592 | 94. |
| 1958 | 2,704 | 4.3 |
| 1959 | 3,074 | 13.7 |
| 1960 | 3,315 | 7.8 |
| 1961 | 3,380 | 2.0 |
| 1962 | 3,670 | 8.6 |
| 1963 | 4,243 | 15.6 |
| 1964 | 4,609 | 8.6 |

# NITRIC ACID MANUFACTURE

## CHEMISTRY OF THE PROCESS

Nitric acid in the United States is produced by the ammonia oxidation process, which entails three principal steps:

One volume of anhydrous ammonia gas is mixed with about nine volumes of hot air and passed through a pad composed of several layers of platinum-rhodium wire-mesh catalyst at high temperature. Nitric oxide (NO) forms according to equation (*1*).

$$4\,NH_3 + 5O_2 = 4NO + 6\,H_2O \qquad (1)$$

When the NO stream is cooled, the NO reacts with oxygen remaining in the mixture to form nitrogen dioxide ($NO_2$) and the dimer, nitrogen tetroxide ($N_2O_4$).

$$2\,NO + O_2 = 2\,NO_2 \rightleftarrows N_2O_4 \qquad (2)$$

The composition of the equilibrium mixture (often referred to as nitrogen peroxide) depends upon temperature. At about 600°C, essentially all $N_2O_4$ is dissociated to $NO_2$. The $NO_2$ is cooled further and is passed to an absorber, where it reacts with water to produce an aqueous solution of nitric acid containing 50 to 60 percent $HNO_3$, depending upon temperature, pressure, absorption stages, and concentration of $NO_2$ entering the absorber system.

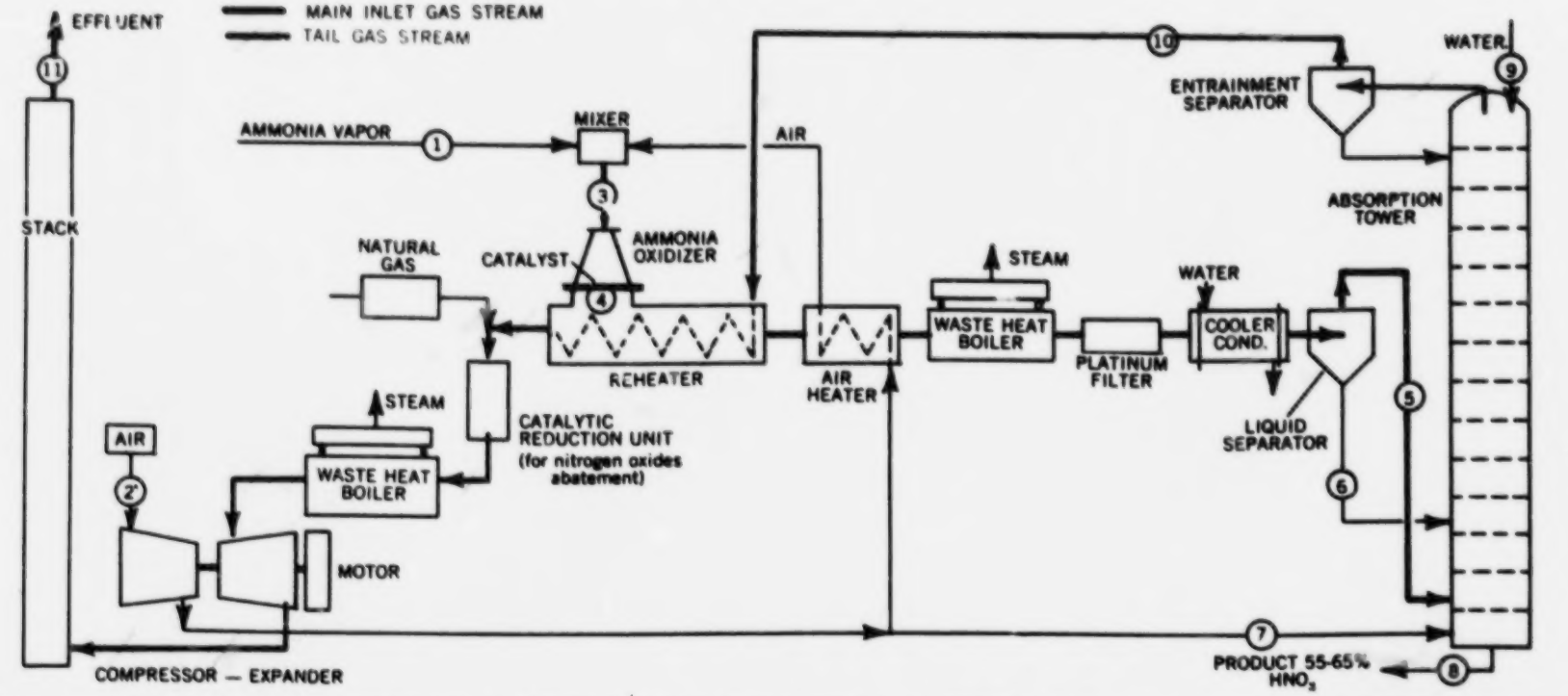
$$3\,NO_2 + H_2O = 2\,HNO_3 + NO \qquad (3)$$

Note that in reaction (*3*) for every two molecules of nitric acid produced there is formed one molecule of nitric oxide, which must be re-oxidized to $NO_2$ according to reaction (*2*) for the absorption reaction to continue. For this purpose secondary air must be supplied to the absorption system. The reaction to form nitric acid is never quite complete on a commercial scale, and a small quantity of nitrogen oxides is inevitably present in the waste gas discharged from the absorption column. The loss is kept to a minimum by proper absorber design and operating conditions.

## THE PRESSURE PROCESS

In the pressure process, the oxidation of ammonia and the absorption of the resulting nitrogen oxides are both carried out at about 80 to 120 psig. A typical arrangement of this process, with data on temperatures, pressures, flows, and compositions, is shown in Figure 1.

In this example, oxidation of the ammonia to nitric oxide is accomplished by passing a preheated mixture of 90 percent air and 10 percent ammonia, by volume, through a catalytic converter at a pressure of 112 psig and a temperature of 1,650°F. The catalyst consists of layers of fine wire gauzes, usually 80-mesh, made with 0.003-inch-diameter wire composed of approximately 90 percent platinum and 10 percent rhodium. Contact time with the catalyst is about 1 millisecond, and conversion of the ammonia to nitric oxide and water is about 95 percent complete at these conditions. The remaining 5 percent is lost through dissociation and side reactions. The resulting nitric oxide, oxygen, nitrogen, and water vapor is passed through




| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | AMMONIA | AIR | MIX | CONVERTER PRODUCTS | COOLED GAS | CONDENSATE ACID | SECONDARY AIR | NITRIC ACID PRODUCT | WATER | TAIL GAS | STACK EFFLUENT |
| FLOW, lb/hr | 2,900 | 51,600 | 47,050 | 47,050 | 38,350 | 8,700 | 7,450 | 16,650 | 3,350 | 41,200 | 42,600 |
| TEMPERATURE, °F | 170 | 60 | 450 | 1,650 | 105 | 105 | 450 | 135 | 100 | 85 | 450 |
| PRESSURE, psig | 170 | 0 | 112 | 112 | 98 | 98 | 120 | 95 | 125 | 92 | 0 |
| $NH_3$, Vol % | 100 | — | 100 | 0 | 0 | — | — | — | — | — | — |
| NO, Vol % | — | — | — | 9.3 | 1.1 | — | — | — | — | 0.10 | 0.01 |
| $NO_2$, Vol % | — | — | — | 0 | 6.4 | 1.2 | — | — | — | 0.15 | Nil |
| $O_2$, Vol % | — | 20.8 | 18.7 | 6.3 | — | — | 20.8 | — | — | 3.0 | Nil |
| $H_2O$, Vol % | — | 0.9 | 0.8 | 15.4 | 0.9 | — | 0.9 | — | — | 0.6 | 3.8 |
| $HNO_3$, Wt % | — | — | — | — | — | 40-50 | — | 60 | — | — | — |
| $H_2O$, Wt % | 0.05 | — | — | — | — | 50-60 | — | 40 | 100 | — | — |
| $N_2$, Vol % | — | 78.3 | 17.5 | 69.0 | 91.6 | — | 78.3 | — | — | 96.15 | 94.2 |
| $CO_2$, Vol % | — | | | | | — | | — | — | | 2.0 |

**Figure 1 — Flow diagram of a typical 120-ton-per-day nitric acid plant utilizing the pressure process.**

various arrangements of heat exchangers. A filter at the exit of the heat exchanger train recovers catalyst dust.

Oxidation of nitric oxide to nitrogen dioxide is a continuing process once the gas leaves the converter; however, oxidation is favored by low temperatures, and no significant formation of nitrogen dioxide occurs until the gas enters the cooler condenser. As the gas becomes cooled, water condenses and reacts with the newly formed nitrogen dioxide to produce a weak nitric acid. Cooler condensers are usually designed with sufficient surface and volume to allow for both cooling of the gas and oxidation of nearly all nitric oxide to nitrogen dioxide.

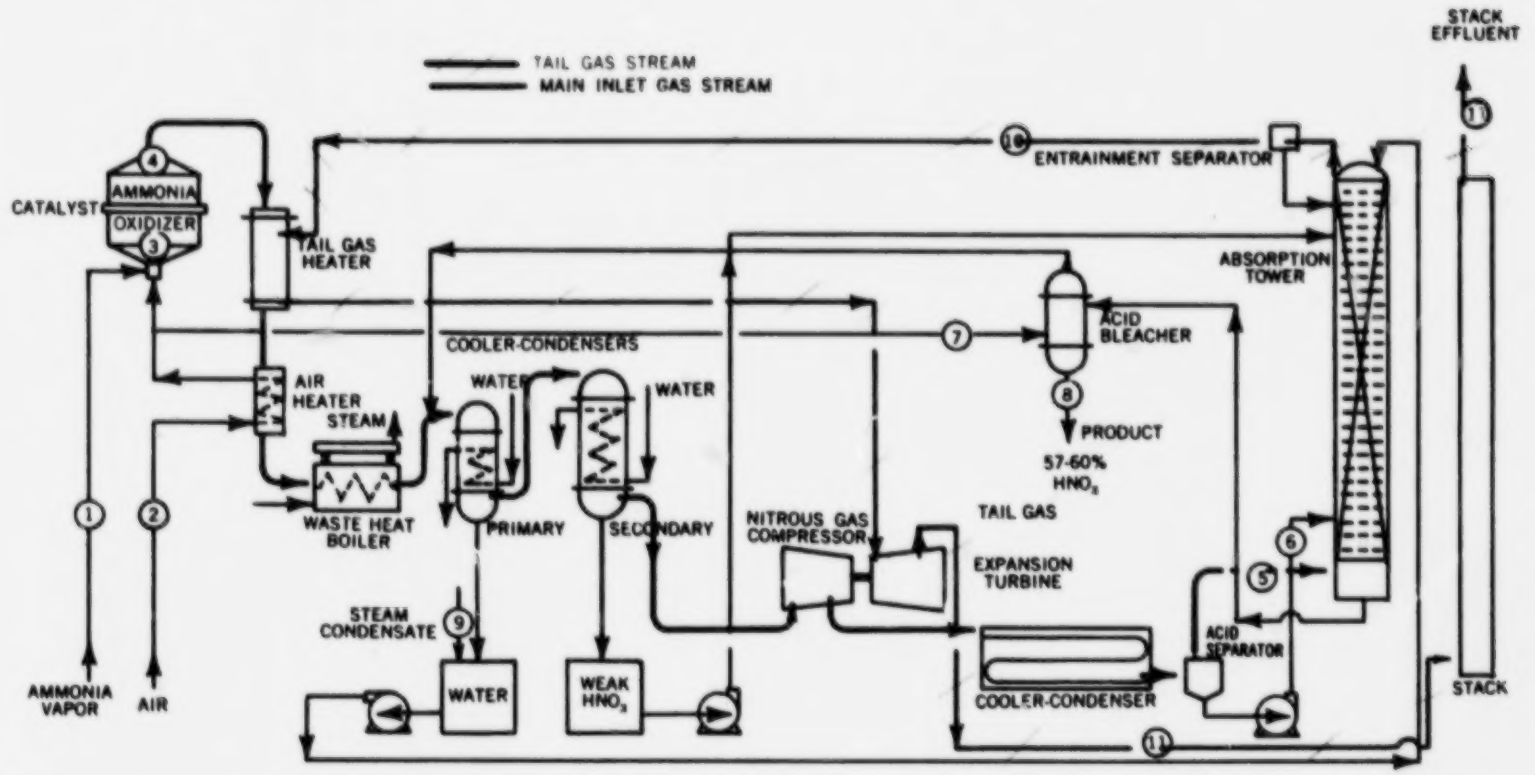
The gas stream leaving the cooler condenser is passed through a cyclone condensate separator before entering the base of the absorber. The separated condensate, which is 40 to 50 percent nitric acid, enters the column at an intermediate point. The absorber contains bubble cap plates to provide intimate countercurrent contact between the aqueous solution and the rising gas stream. Because the absorption of nitrogen dioxide in this solution and its reaction with water to form nitric acid are highly exothermic processes, the tower is provided with internal cooling coils to remove the heat of reaction. Water is fed to the top of the column for absorption, and secondary air enters the bottom of the column to provide oxygen for the conversion of nitric oxide to nitrogen dioxide in the absorber.

Unabsorbed gas, principally nitrogen, leaves the absorption tower at a temperature of about 85°F and is passed through an entrainment separator. The tail gas is then heated by heat exchange with the hot process gases. The energy contained in the resultant hot gas is recovered in a centrifugal expander, which drives the air compressor. The gas leaving the expander is then discharged to the atmosphere. The reheated tail gas may be passed through a catalytic combustion unit or fume abater to reduce nitrogen oxides, as shown in Figure 1, before entering the centrifugal expander.

## COMBINATION AND INTERMEDIATE-PRESSURE PROCESSES

In the combination pressure process, the oxidation of ammonia occurs at pressures from atmospheric to about 30 psig. The resulting oxides of nitrogen are then cooled and generally compressed to about 30 to 50 psig before being absorbed. Figure 2 illustrates the basic process. This system provides the benefits of lower maintenance, reduced catalyst loss, and higher conversion efficiency obtained by operating the ammonia converter at low pressures. Further, it provides the benefits obtained by high-pressure absorption; these include smaller absorber size, greater absorption efficiency, and higher-strength product acid. Such nitric acid plants are not common in the United States; they are mentioned to provide a complete picture of process variations.

The basic chemistry is identical with that encountered in the high pressure systems; i.e. oxidation of ammonia over a catalyst, oxidation of the resulting nitrogen compounds to nitrogen dioxide, and absorption of the resulting oxides in water. Acid strengths up to 70 percent have been obtained with these systems.(4)




| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | AMMONIA | AIR | MIX | CONVERTER PRODUCTS | COOLED GAS | CONDENSATE ACID | SECONDARY AIR | NITRIC ACID PRODUCT | WATER | TAIL GAS | STACK EFFLUENT |
| FLOW, lb/hr | 2,880 | 53,550 | 45,680 | 45,680 | 52,730 | 3,700 | 10,750 | 16,650 | 3,600 | 43,450 | 43,450 |
| TEMPERATURE, °F | 170 | 60 | 270 | 1,550 | 160 | 95 | 250 | 80 | 60 | 85 | 450 |
| PRESSURE, psig | 5 | 5 | 5 | 4 | 40 | 40 | 5 | 0 | 50 | 40 | 0 |
| $NH_3$, Vol % | 100 | — | 10.2 | 0 | 0 | — | — | — | — | — | — |
| NO, Vol % | — | — | — | 9.6 | 5.1 | — | — | — | — | 0.10 | 0.13 |
| $NO_2$, Vol % | — | — | — | 0 | 3.2 | Nil | — | — | — | 0.10 | 0.07 |
| $O_2$, Vol % | — | 20.8 | 18.7 | 6.2 | 8.0 | — | 20.8 | — | — | 4.0 | 4.0 |
| $H_2O$, Vol % | — | 0.9 | 0.8 | 15.4 | 4.6 | — | 0.9 | — | — | 1.5 | 1.5 |
| $N_2$, Wt % | — | 78.3 | 70.3 | 68.8 | 79.1 | — | 78.3 | — | — | 94.3 | 94.3 |
| $HNO_3$, Wt % | — | — | — | — | — | 15.0 | — | 60.0 | — | — | — |
| $H_2O$, Wt % | <0.5 | — | — | — | — | 85.0 | — | 40.0 | 100 | — | — |

**Figure 2 — Flow diagram of a typical 120-ton-per-day nitric acid plant utilizing the combination pressure process.**

The intermediate-pressure plant operates at pressures of 20 to 60 psig throughout the plant. The basic process is identical to the high-pressure system except that, because of the lower pressure, additional absorber volume is required. A series of water-cooled horizontal drum absorbers have been used for absorption in this type of plant.(5)

## ATMOSPHERIC-PRESSURE PROCESS

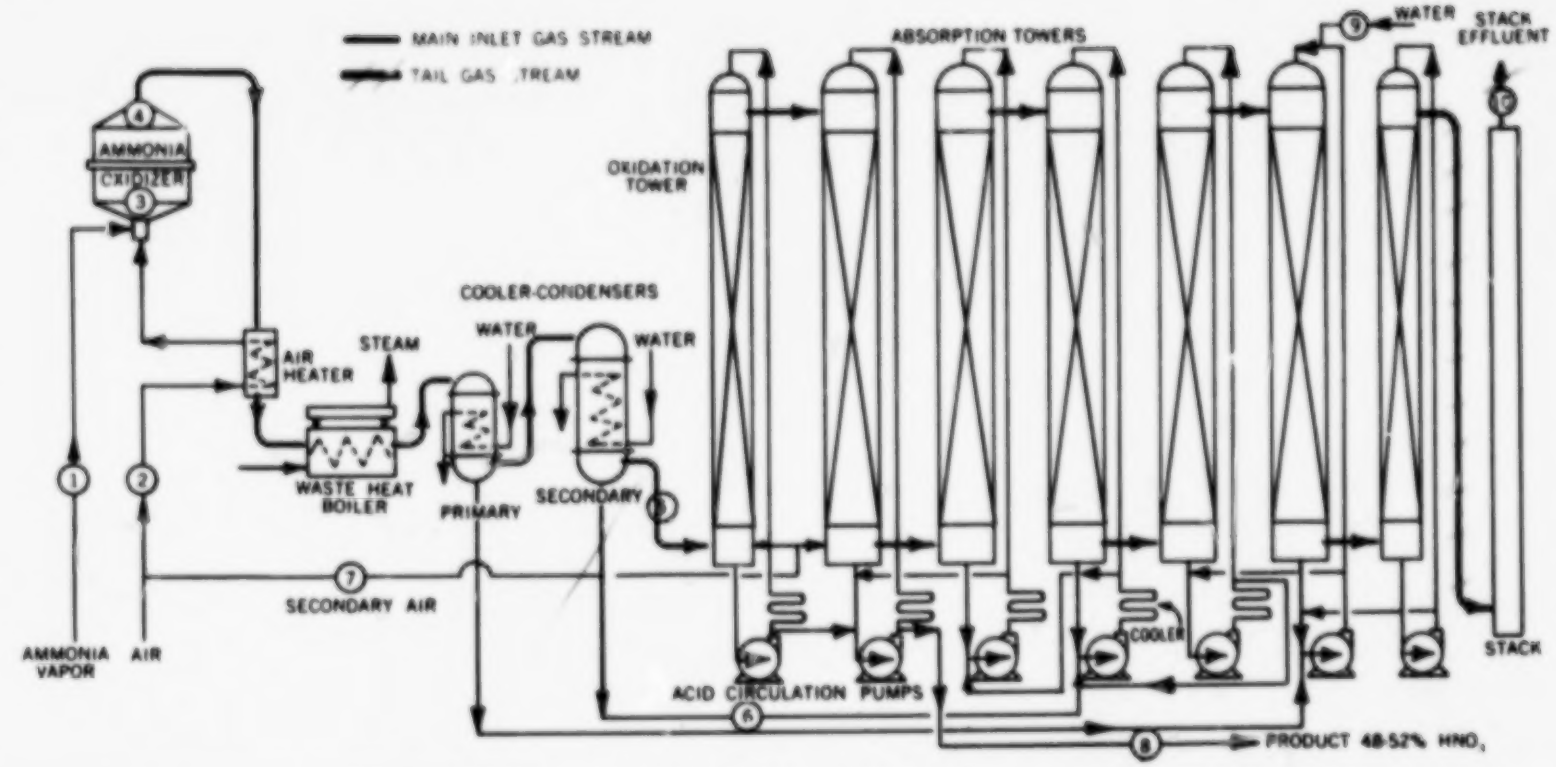
Because acid-resistant materials were not available, absorption towers in all of the early nitric acid plants were constructed of brick, which could not withstand high pressures. The absorption towers therefore had to operate at atmospheric pressure. With the advent of acid-resistant steel alloys capable of withstanding high pressures, and with the demand for higher-strength nitric acid, the atmospheric-pressure plant became outmoded.

Some of these early plants are still in existence today; however, most are on a standby basis and are not normally in operation. Operation at atmospheric pressure generally results in a high initial investment because of the large absorber volume required. Maintenance and operating problems and costs are minimal, however.

The basic chemistry of the atmospheric-pressure process for the production of nitric acid by ammonia oxidation is also identical to that of the pressure process except that all reactions occur at essentially atmospheric pressure.

As shown in Figure 3, the ammonia-air mixture reacts across a 90:10 platinum-rhodium gauze catalyst at about 1550°F and is oxidized to nitric oxide. This gas stream is cooled, and the resulting very weak acid condensate is fed into the weak end of the absorption system. A typical analysis of the cooled gas at this point is 6.4 percent NO, 4.0 percent $NO_2$, 5.6 percent $H_2O$, 4.7 percent $O_2$, and the balance $N_2$. To promote the further oxidation of NO to $NO_2$ the gas is next passed into large oxidation towers, where residence time is sufficient for the substantial completion of the oxidation to $NO_2$. The gas stream then passes into a series of absorption towers. Because of the poor absorption characteristics of nitrogen dioxide in water at atmospheric pressure and the very slow rate of re-oxidation of NO to $NO_2$, a large absorption volume is required, about 70 times the volume required at a pressure of 110 psig. This is because the rate of oxidation of nitric oxide to nitrogen dioxide varies directly with the square of the pressure, and operation at atmospheric pressure thus requires greatly increased time for oxidation to occur. Product acid concentrations range from 40 to 50 percent.

Conversion of ammonia to nitric oxide at atmospheric pressure is higher than at elevated pressures (about 98 percent versus 95.5 percent). Compared to a high-pressure-type ammonia converter, the atmospheric unit has a much larger cross sectional area of catalyst and employs a larger quantity of catalyst per daily ton of capacity. Catalyst life is improved largely because of the lower temperature at which the catalyst operates (1550°F). Gauzes are replaced only every few months, whereas in the high-pressure converter they must be replaced every few weeks.




| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| | AMMONIA | AIR | MIX | CONVERTER PRODUCTS | COOLED GAS | CONDENSATE ACID | SECONDARY AIR | NITRIC ACID PRODUCT | WATER | STACK EFFLUENT |
| FLOW, lb/hr | 2,850 | 54,250 | 46,100 | 46,100 | 44,350 | 1,750 | 11,000 | 18,850 | 5,750 | 45,000 |
| TEMPERATURE, °F | 100 | 60 | 270 | 1,550 | 95 | 95 | 60 | 80 | 100 | 85 |
| PRESSURE, psig | 5 | 5 | 5 | 4 | 3 | — | — | — | 40 | 0 |
| $NH_3$, Vol % | 100 | — | 10.0 | 0 | 0 | — | — | — | — | — |
| NO, Vol % | — | — | — | 9.6 | 6.4 | — | — | — | — | 0.1 |
| $NO_2$, Vol % | — | — | — | 0 | 4.0 | Nil | — | — | — | 0.2 |
| $O_2$, Vol % | — | 20.8 | 18.7 | 6.2 | 4.7 | — | 20.8 | — | — | 4.0 |
| $H_2O$, Vol % | — | 0.9 | 0.8 | 15.4 | 5.6 | — | 0.9 | — | — | 4.2 |
| $HNO_3$, Wt % | — | — | — | — | — | 25.7 | — | 50.0 | — | — |
| $H_2O$, Wt % | < 0.5 | — | — | — | — | 74.3 | — | 50.0 | 100 | — |
| $N_2$, Wt % | — | 78.3 | 71.5 | 68.8 | 79.3 | — | 78.3 | — | — | 91.5 |

**Figure 3 — Flow diagram of a typical 120-ton-per-day nitric acid plant utilizing the atmospheric pressure process.**

An additional benefit is gained because ammonia evaporates at -28°F at atmospheric pressure. Thus, no preheating is required to evaporate the liquid ammonia, and its refrigerating value can be used advantageously to cool the absorption system.

## OTHER PROCESSES

The electric-arc process has found limited use. In this process, air is passed through an electric arc and at the prevailing high temperatures about 1 or 2 percent of the nitrogen in the air is converted to nitric oxide. The gases are rapidly cooled and oxidized to nitrogen dioxide.

Newer processes include the Wisconsin process (6) and nuclear nitrogen fixation. (7) In the Wisconsin process about 1 percent of the nitrogen in the air is converted to nitric oxide by heating the air to 4,000°F in a pebble furnace. A double bed of magnesia pebbles preheats the incoming air and also rapidly chills the combustion products and thus prevents dissociation of the NO. The product, containing about 2 percent NO, is then concentrated in silica gel columns. Silica gel is used first to dehydrate the gas stream and catalyze the oxidation of NO to $NO_2$. The $NO_2$ is then specifically adsorbed on silica gel and finally released from the silica gel in concentrated form by heating the bed. The resulting gas is absorbed in water and can be used to make a 60 percent acid.

The nuclear nitrogen fixation process is not nearly so well developed as the Wisconsin process, and neither process is in commercial use today. Yields of 5 to 15 percent nitrogen oxides have been obtained by exposing compressed air at 150 psi and 400°F to radiation from uranium-235. Nitrogen and oxygen molecules are oxidized and decomposed by fission products and alpha and gamma radiation.

## ACID CONCENTRATION PROCESSES

The major portion of the 55 to 65 percent nitric acid produced by the ammonia oxidation process is consumed at this strength. As previously mentioned, much of it is used directly in the manufacture of ammonium nitrate. There remains, however, a fairly substantial requirement for high-strength (95 to 99 percent) nitric acid, which is obtained by concentrating the 55 to 65 percent $HNO_3$.

The nitric acid—water system forms a maximum boiling azeotrope at a concentration of 68.4 percent $HNO_3$ at atmospheric pressure; consequently, nitric acid can not be concentrated beyond this strength by simple fractional distillation. The distillation must therefore be carried out in the presence of a dehydrating agent. Concentrated sulfuric acid is most commonly used for this purpose, although 70 to 75 percent magnesium nitrate is also used to a limited extent.

Figure 4 is a simplified diagram of a typical nitric acid concentration unit. As shown, the process consists of feeding strong sulfuric acid and 60 percent nitric acid to the top of a packed dehydrating column, through which it flows downward countercurrent to ascending vapors. Concentrated nitric acid leaves the top of the column as 98 percent vapor containing a

small amount of $NO_2$ and $O_2$ resulting from dissociation of nitric acid. The vapors pass to a bleacher and countercurrent condenser system to effect condensation of strong nitric acid and separation of the oxygen and nitrogen oxides. These cooled noncondensable gases flow to an absorption column for recovery of the nitrogen oxides as weak nitric acid in much the same manner as in the pressure-process nitric acid plants. Auxiliary air is added to the bottom of the column, and inert gases and unreacted nitrogen oxides are vented to the atmosphere from the top of the column. The entire process operates at approximately atmospheric pressure.

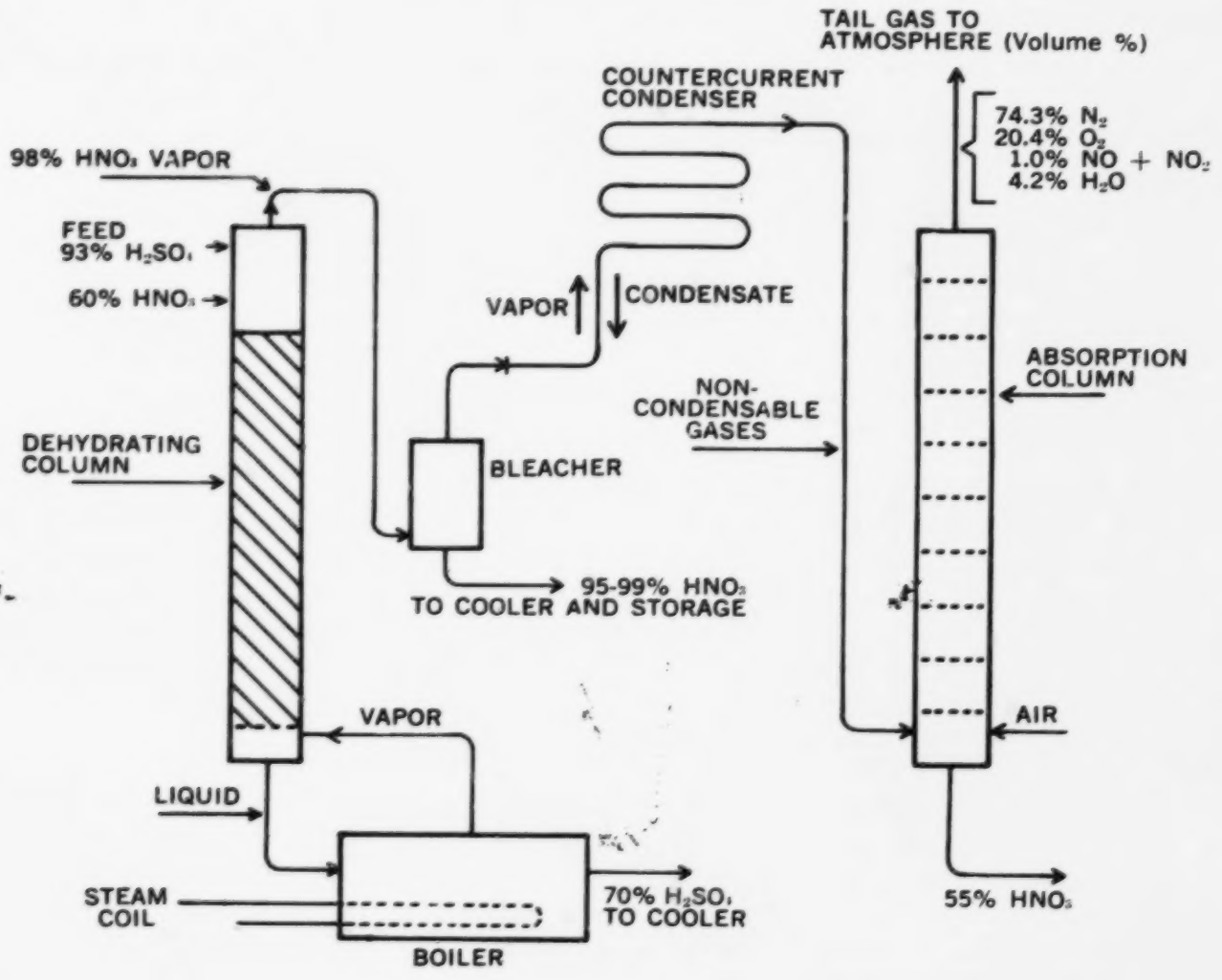



Figure 4 — Nitric acid concentrating unit.

## ABATEMENT METHODS AND EQUIPMENT

The emission of nitrogen oxides may be reduced by catalytic reduction with certain fuels and by absorption, adsorption, and flaring. Catalytic reduction is by far the most widely used method of abatement.

### Catalytic Reduction Systems (*8, 9*)

Catalytic reduction is particularly suited to the pressure ammonia oxidation process, in which the absorption tower tail gas is of uniform composition and flow, is under pressure, and can be reheated by heat exchange to the necessary reduction-system feed temperature. Efficiencies above 90 percent



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are possible, and in addition a significant economic return can be realized through recovery of heat generated in the catalytic recovery unit.

In operation the tail gases from the absorber are heated to the necessary catalyst ignition temperature, mixed with a fuel such as hydrogen or methane (natural gas), and passed into the reactor and over a bed of catalyst. A number of reactions take place resulting in the dissociation and decompostition of nitrogen oxides:

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O \quad (4)$$

$$CH_4 + 4\,NO_2 = 4\,NO + CO_2 + 2\,H_2O \quad (5)$$

$$CH_4 + 4\,NO = 2\,N_2 + CO_2 + 2\,H_2O \quad (6)$$

Reactions (4) and (5) proceed rapidly, with evolution of considerable heat. Since the nitrogen dioxide is all converted to nitric oxide in reaction (5), the gas is now colorless even though there is yet no substantial destruction of nitric oxide. The reaction of further amounts of natural gas with the nitric oxide in accordance with reaction (6), which takes place more slowly, results in decomposition of the nitric oxide to nitrogen. When this reaction is complete, total abatement is achieved.

A typical catalytic reduction unit is shown in Figure 5; the arrangement of such a unit in conjunction with a pressure-process nitric acid plant is shown in Figure 1. Temperatures and compositions are shown for illustrative purposes. In practice, operating conditions are governed by the kind of fuel employed, the gas composition, and the type of catalyst. When hydrogen is used as fuel, the minimum ignition temperature is about 290°F and the temperature rise is approximately 300°F for each percent of oxygen in the tail gas. With natural gas as fuel, minimum ignition temperature is about 850°F and the temperature rise is 270°F for each percent of oxygen.

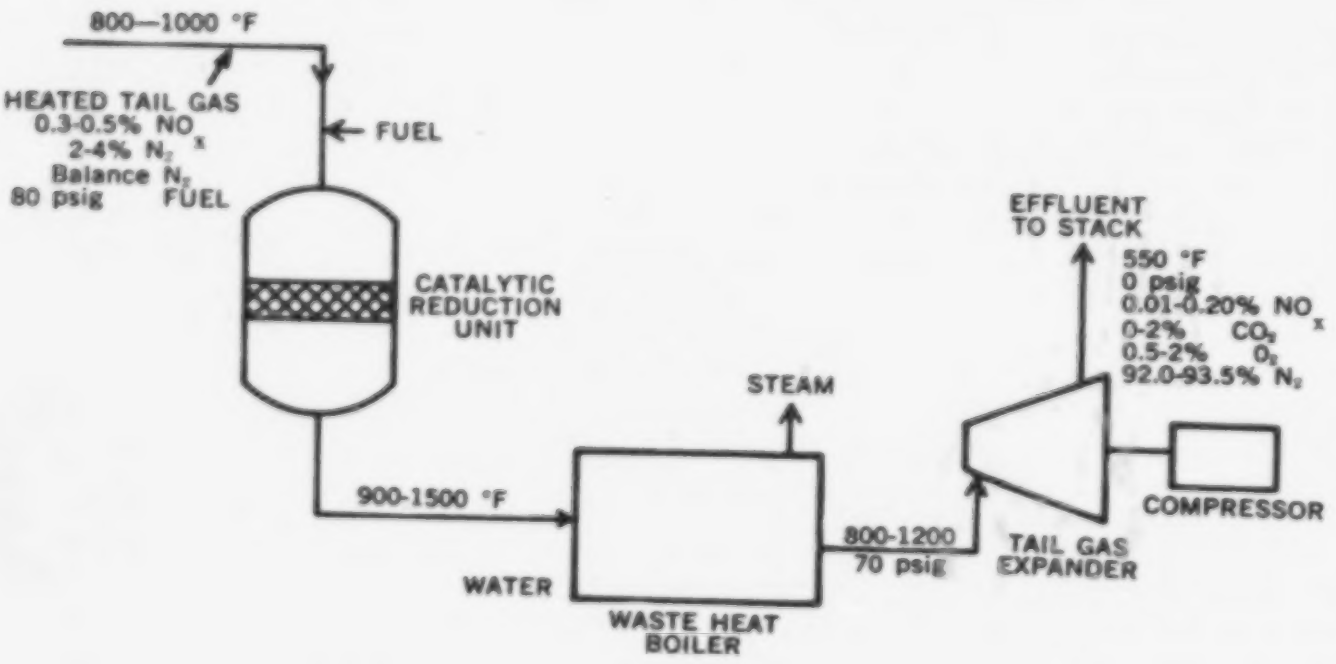


Figure 5 — Typical nitric acid plant tail gas catalytic reduction unit utilizing natural gas.

Usually the catalyst consists of 0.5 percent platinum or palladium on a support such as woven Nichrome ribbon or ceramic material having a pelleted or honeycomb structure. The honeycomb support offers the advantage of low pressure drop. The catalyst will withstand temperatures as high as 1,400 to 1,500°F, which is also the approximate upper temperature limit for the reaction vessels used in this service.

In a single-stage reduction unit, increasing the amount of fuel raises the temperature of the gas as reactions (4) and (5) take place. Generally, the temperature limit of about 1,500°F is reached before all oxygen has reacted with the fuel, especially when natural gas is used. Under these conditions the effluent is a colorless gas in which the nitrogen oxides are present only as nitric oxide. As shown in Figures 1 and 5, the heat thus generated can be recovered in a waste heat boiler and can also be recovered as energy in driving the tail-gas expansion turbine.

Because temperature limits the extent of reaction in a single-stage reactor, a two-stage reduction process may be required to split the heat load. This would permit use of excess fuel, or operation on the reducing side, whereby all oxygen in the tail gas is reacted and the nitrogen oxides are decomposed in accordance with equation (6). The stack effluent will contain 0.01 to 0.02 percent or less of nitrogen oxides. It is technically possible to carry out essentially full reduction and decomposition of the nitrogen oxides (for example, to 0.01 to 0.02 percent $NO_x$) in a single stage if the oxygen content of the absorber tail gas is kept well below the usual 3 percent so as to reduce the heat of reaction. Under these conditions, however, there will be a loss in absorption efficiency in the nitric acid plant with a consequent operating-cost penalty.

Performance of existing catalytic units varies widely and depends on the method of operation. One operator may desire maximum reduction of the nitrogen oxides, another may aim for a colorless plume, and a third, for maximum heat generation. These variations are obtained by changes in the amount and type of fuel, the amount of catalyst, oxygen content of the tail gas, operating temperatures, and reaction time. The basic equipment design is also a governing factor. Normally, a colorless effluent is accepted as an indication of proper functioning but not necessarily of a reduction in nitrogen oxides. In one known instance in which 1 percent methane was reacted with a tail gas containing 1,100 ppm $NO_2$, 1,900 ppm NO, and 4 percent $O_2$, the exit gases contained 260 ppm $NO_2$, and 2,300 ppm NO. (*10*) The exit gas was nearly colorless, but its nitrogen oxides content was reduced only slightly. As previously pointed out, the high oxygen content of the tail gas and the consequent high temperature rise in the reactor may have limited the quantity of fuel used to less than the stoichiometric amount needed to react with all the oxygen and nitrogen oxides.

The cost of a catalytic tail-gas reduction unit, including catalyst, varies from $1 to $2 per scfm of tail gas. Depending on the amount of steam produced and on costs of fuel, the systems will recover a substantial portion of their capital cost. This steam can be used to furnish part of the power to drive the nitric acid plant air compressor or it may be used as plant process steam.

Large nitric acid plants equipped with catalytic tail-gas reduction units may use no outside power after startup. The heat generated in the oxidation of ammonia and in catalytic abatement combine to provide all the energy necessary to drive the large air compressor. (*11*)

Ammonia can also be used as a fuel for the catalytic reduction of nitrogen oxides. It differs from other fuels in that it reacts selectively with NO and $NO_2$ to form nitrogen without simultaneously reacting with the oxygen in the tail gas. As a result, temperature rise in the catalytic reactor is very small. A platinum catalyst supported on ceramic pellets is employed. The reactions are

$$4\ NH_3 + 3\ NO_2 = 3\tfrac{1}{2}\ N_2 + 6\ H_2O \quad (7)$$
$$2\ NH_3 + 3\ NO = 2\tfrac{1}{2}\ N_2 + 3\ H_2O \quad (8)$$

These reactions are carried out within the temperature range 410 to 520°F. Below 410°F there is a chance that ammonium nitrate would be formed. Above 520°F, oxides of nitrogen are formed by the typical ammonia reaction. In one known commercial installation, ammonia is used as the fuel in catalytic reduction of nitrogen oxides. The potential presence of ammonium salts in the effluent could be a deterrent to its use where the gas stream is subsequently used to drive a turbine expander.

**Absorption Systems**

Various types of absorption towers, in which water is the absorbing medium, can be used where the nitrogen oxide content, as $NO_2$, of the effluent stream is relatively high, perhaps 2 to 8 percent. Such a system functions like an atmospheric-pressure nitric acid plant and is suitable for application in the recovery and reduction of nitrogen oxides evolved from nitration or nitric acid oxidation processes.

Best performance can be realized with a gas stream of steady flow and uniform composition. Water absorbers are not very effective for reducing emissions from nitric acid manufacturing plants, since these gas streams represent the effluent from aqueous absorption systems and the nitrogen oxides concentration, averaging 0.3 percent, is too low for efficient absorption. (*12*)

Absorption in alkaline solutions, such as sodium carbonate or sodium hydroxide, is more effective than in water. Under proper feed stream compositions, nitrate and nitrite salts can be formed according to the following reactions:

$$2\ NaOH + 3\ NO_2 \longrightarrow 2\ NaNO_3 + NO + H_2O \quad (9)$$
$$2\ NaOH + NO + NO_2 \longrightarrow 2\ NaNO_2 + H_2O \quad (10)$$

An alternate scrubbing system utilizes two stages, with water in the first stage and sodium hydroxide in the second, again yielding nitrite and nitrate salts. Disposing of the byproduct salt solutions may be a problem.

**Adsorption Systems**

Nitrogen dioxide may be removed by adsorption on activated charcoal or silica gel. Adsorption on silica gel is actually the basis of the Wisconsin process for recovery of $NO_2$, which is present to the extent of 1 to 2 percent

in the gases from the thermal fixation process. The method has not been used commercially for reducing emissions of nitrogen oxides.

**Flaring**

Passing the gases that contain nitrogen oxides through a combustion chamber or flame will usually reduce the nitrogen oxides to nitric oxide and thereby provides a colorless emission. The extent of nitrogen oxides destruction, to nitrogen, is influenced by the kind of burner or flare, the type of fuel, and the initial concentration of nitrogen oxides in the waste gas. The performance to be realized for any given set of conditions must be determined experimentally.

Flaring is too costly for the abatement of effluents in nitric acid plants because of the large volume of gas and low initial nitrogen oxides concentration. However, where there is intermittent discharge of nitrogen oxides in concentrations of 1 percent or more, flaring may be the best means of abatement.

**Tall Stacks**

Tall stacks aid in the dispersion of nitrogen oxide gases. Increased temperature and velocity of the gases increase effective stack height and further aid dispersion. Hot gases from adjacent processes may be added to the effluent stack, thus raising the temperature and diluting the emission.

Some European plants use a venturi device on top of a tall stack. The induction created by the discharge of tail gas through the venturi brings about a 5:1, or greater, dilution of the effluent with air before it enters the atmosphere. There is at least one such installation in the United States.

# EMISSIONS FROM NITRIC ACID PROCESSES

## NITRIC ACID MANUFACTURE

The main source of atmospheric emissions from the manufacture of nitric acid is the tail gas from the absorption tower, which contains unabsorbed oxides of nitrogen. These oxides are largely in the form of nitric oxide and nitrogen dioxide. In addition, trace amounts of nitric acid mist are present in the gases as they leave the absorption system. In the pressure process these gases are reheated for power recovery purposes and discharged to the atmosphere at 400 to 500°F; any nitric acid mist present is then changed to its vapor state prior to discharge into the atmosphere. In the atmospheric system, tail gases discharged to the atmosphere are cold, and therefore any entrained particles of nitric acid in this gas stream would appear as a mist. The quantity depends upon extent of entrainment and the efficiency of entrainment separators.

The tail gas is reddish-brown; the intensity of the color depends on the concentration of nitrogen dioxide present. Data in Table 2 show that concentrations of 0.13 to 0.19 percent by volume of nitrogen dioxide produce a definite color in the exit plume. Effluent gases containing less than 0.03 percent nitrogen dioxide are essentially colorless. Note that nitric oxide, as distinguished from nitrogen dioxide, is colorless.

Table 2 presents emission and operating data from 12 plants. Emissions range from 0.1 to 0.69 volume percent nitrogen oxides, with an average of 0.37. Limited data indicate that nitrogen dioxide accounts for approximately ⅓ to ½ of these values, the balance being nitric oxide.

Except for Plant 1, all plants listed in Table 2 were of similar design and were operated at absorber pressures of 72 to 90 psig and at temperatures of about 90°F at the absorber outlet. All of the plants were producing acid in the 55 to 60 percent range and were generally operating near nominal capacity.

Plant 1 had been modified by the addition of another acid bleacher and of 12 plates to the top of the absorber. Hot bleach air was injected into the cooler-condenser, and changes had been made in the process piping in an effort to produce acid more efficiently. This plant is thus not typical of standard design.

In Plant 2 and probably Plant 8 leaks in the tail-gas reheater account for the high emission values. If the values for Plants 1, 2, and 8 are excluded, the average emission of nitrogen oxides is 0.32 percent.

Emission values for Plants 11 and 12 show that a decrease of 40 to 60 percent in oxygen tends to raise the nitrogen oxide content of the tail gas by about 30 to 50 percent (compare with values for Plant 10.) The very low nitrogen oxides content of the tail gas in Plant 3 is due partly to the lower absorption-tower temperature.

Nitrogen dioxide was measured only at Plants 1 and 2; it constituted 54 and 28 percent, respectively, of the total nitrogen oxides content. At Plant 2 the leak in the tail-gas reheater caused gas rich in nitric oxide (NO) from the ammonia converter to leak into the tail-gas stream. The percent nitrogen dioxide was thus a smaller part of the total.

TABLE 2

EMISSION AND OPERATING DATA FOR NITRIC ACID PLANTS
WITHOUT WASTE GAS TREATMENT EQUIPMENT

| Plant number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11[e] | 12[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Rated capacity, tons/day (100% acid basis) | 55 | 55 | 60 | 120 | 120 | 120 | 120 | 180 | 200 | 265 | 700 | 750 |
| Normal acid strength, % | 60 | 60 | 57.5 | 57 | 57 | 57 | 57 | 55 | 57.5 | 56 | 55.7 | 55 |
| Percent of rated capacity | 88 | 72 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Ammonia feed rate, lb/hr | | | 1454 | 2750 | 2750 | 2750 | 2750 | 4000 | 4740 | 6670 | 17,500 | 18,750 |
| Ammonia oxidation pressure, psig | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 105 | 115 | 120 | 120 |
| Absorption column exit pressure, psig | 72 | 75 | 88 | 90 | 90 | 90 | 90 | 80 | 85 | 89 | 90 | 80 |
| Absorption column exit temp., °F | 96 | 95 | 80 | 90 | 90 | 90 | 90 | 95 | 90 | 100 | | 90 |
| Stack gas rate, Mscfm[a] | 3.5 | 3.4 | 5.3 | 10.5 | 10.5 | 10.0 | 10.0 | 15.5 | 16.5 | 21.8 | 59 | 57.6 |
| Total nitrogen oxides in stack gas, vol %[b] | 0.24 | 0.69[d] | 0.1 | 0.31 | 0.34 | 0.34 | 0.35 | 0.60 | 0.28 | 0.30 | 0.45 | 0.40 |
| Nitrogen dioxide in stack gas, vol % | 0.13 | 0.19 | | | | | | | | | | |
| Oxygen in stack gas, vol % | 4.1 | 4.5 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 4.0 | 3.0 | 4.0 | 1.5 | 2.5 |
| Total nitrogen oxides emitted, tons/day[c] | 0.8 | 2.2 | 0.5 | 3.0 | 3.3 | 3.1 | 3.2 | 8.6 | 4.3 | 6.0 | 24.5 | 21.3 |
| Pounds of nitrogen oxides emitted per ton of acid produced (100% basis)[c] | 33 | 111 | 17 | 50 | 55 | 52 | 53 | 96 | 43 | 45 | 70 | 57 |
| Plume opacity | med. | heavy | light | med. | med. | med. | med. | med. | | med. | | |
| Plume color | light brown | dark brown | light orange | light brown | light brown | light brown | light brown | yellow | | light orange | light brown | brown yellow |

[a] All volumes corrected to 32°F and 29.9 in. Hg.
[b] Does not include $N_2O$.
[c] Calculated on the basis that all the nitrogen oxides are nitrogen dioxide.
[d] Suspected leak in tail gas reheater.
[e] More than one unit.

Table 3 presents emission and operating data for 11 plants equipped with catalytic combustors for the reduction and removal of nitrogen oxides normally present in absorption-column tail gases. The general arrangement of this equipment is as shown in Fig. 1. Hydrogen, natural gas, or a mixture of the two are used as fuels. The data show the composition of the tail gas leaving the absorber and of the effluent leaving the catalytic waste gas combustor. Catalytic waste gas treatment reduced the total nitrogen oxides emission by 36 to 99.8 percent. In all cases the stack effluent was clear and colorless, indicating reduction of all nitrogen dioxide to nitric oxide. In most cases there was substantial, if not total, removal of oxygen by combustion with the fuel.

Only at Plant 22 was gas composition data available to show both total nitrogen oxides ($NO + NO_2$) and nitrogen dioxide. At this plant the catalytic combustor reduced the nitrogen dioxide content of the absorber tail gas by 92 percent and reduced the total nitrogen oxides content by 61 percent. As in the other examples, the stack effluent was clear and colorless.

Alkaline scrubbers also reduce the emission of nitrogen oxides effectively. Data for five plants are presented in Table 4. The two-stage sodium hydroxide-water scrubber (Plants 24 and 25) performed exceptionally well, with an overall reduction of 91 percent in nitrogen oxides content. Scrubbing with sodium carbonate solution, as illustrated by data on Plants 26 and 27, left 0.4 percent nitrogen oxides in the gases after treatment. Efficiency of scrubbing in this case cannot be evaluated because no data were available on the composition of the tail-gas stream entering the scrubber. The data on Plant 28 show a very high (2.5 percent) nitrogen oxides concentration in gases entering the sodium carbonate scrubber; this high value might indicate that the principal purpose of the scrubber here was to produce nitrite and nitrate salts rather than to reduce emissions below the usual 0.15 to 0.40 percent nitrogen oxides concentration characteristic of untreated tail gas.

Figure 6 shows the pounds of total nitrogen oxides calculated as nitrogen dioxide emitted per hour for various sized plants and various tail-gas concentrations.

Small amounts of acid mist may be present in the emissions from some plants. A small quantity of entrained acid is generally present in the gases leaving the absorption system. In the pressure process, the tail gases are reheated and expanded before being released to the atmosphere at 400 to 500°F; this treatment results in vaporization of any traces of acid mist that may have been present in the gases from the absorber. In the atmospheric process the cold tail gas discharged to the atmosphere may contain some entrained acid mist, the quantity depending on the efficiency of entrainment separators prior to discharge.

Based on typical operating data, the tail gas from the usual pressure process may be considered to have the following average composition:

| | |
|---|---|
| Total nitrogen oxide ($NO + NO_2$) | 0.3% |
| Oxygen | 3.0% |
| $H_2O$ | 0.7% |
| $N_2$, etc. | Balance |

TABLE 3
EMISSION AND OPERATING DATA FOR NITRIC ACID PLANTS HAVING CATALYTIC WASTE GAS TREATMENT EQUIPMENT

| Type of fuel[a] | | NG | $H_2$ | NG | $H_2$ | NG | 75% $H_2$ 25% NG | $H_2$ | 75% $H_2$ 25% NG | NG | NG | NG |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plant number | | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
| Rated capacity, tons/day (100% acid basis) | | 110 | 120 | 140 | 150 | 170 | 185 | 220 | 230 | 280 | 340 | 350 |
| Normal acid strength, % | | 51 | 60 | 57 | 56 | 53 | 57 | 57 | 58 | 57 | 57 | 57 |
| Percent of rated capacity | | 127 | 100 | 100 | 100 | 106 | 100 | 95 | 119 | 110 | 100 | 100 |
| Ammonia feed rate, lb/hr | | 3346 | 2880 | 3500 | 3675 | 4100 | 4471 | 6150 | 6700 | 6800 | 8600 | 8460 |
| Ammonia oxidation pressure, psig | | 105 | 120 | 110 | 105 | 20 | 102 | 105 | 115 | 132 | 98 | 108 |
| Absorption column exit pressure, psig | | 70 | 94 | 90 | 80 | 24 | 79 | 82 | 80 | 100 | | 92 |
| Absorption column exit temp., °F | | 85 | 78 | 100 | 90 | | 83 | 86 | 98 | 65 | | 104 |
| Tail gas rate, Mscfm[b] | | 10.9 | 9.3 | 11.3 | 11.7 | 13.7 | 14.5 | 20 | 20.5 | 21.2 | 27.1 | 28.6 |
| Gas temperature and compositions before treatment equipment, vol. % | Temperature, °F | 840 | 375 | | 502 | 250 | 660 | | 570 | | | |
| | Oxygen | 3.5 | 2.4 | 1.5 | 2.2 | 3.0 | 2.5 | 2.7 | 1.6 | 2.1 | 1.9 | 3.0 |
| | Total nitrogen oxides[c] | 0.21 | 0.10 | 0.50 | 0.3 | 0.22 | 0.3 | 0.30 | 0.54 | 0.36 | 0.54 | 0.2 |
| | Nitrogen dioxide | | | | | | | | | | 0.26 | |
| Gas temperature and compositions after treatment equipment, vol. % | Temperature, °F | 1250 | 915 | 1500 | 1120 | 900 | 1190 | | 930 | | | 1250 |
| | Oxygen | | None | None | None | 1.9 | None | 0.5 | None | 0.9 | 1.7 | 1.73 |
| | Total nitrogen oxides | 0.04 | <0.0002 | 0.015 | 0.01 | 0.14 | 0.005 | 0.1 | 0.008 | 0.04 | 0.21 | 0.044 |
| | Nitrogen dioxide | | | | | | | | | | 0.02 | |
| | Carbon dioxide | | None | 1.0 | Nil | 0.88 | | Nil | | 0.67 | 0.6 | 0.74 |
| Percent reduction in nitrogen oxides | | 81 | 99.8 | 97 | 97 | 36 | 98 | 67 | 98.5 | 89 | 61 | 78 |
| Total nitrogen oxides emitted, tons/day[d] | | 0.40 | Nil | 0.15 | 0.11 | 1.8 | 0.07 | 1.85 | 0.15 | 0.78 | 5.25 | 1.16 |
| Pounds of nitrogen oxides emitted per ton of acid produced (100% basis)[d] | | 5.7 | Nil | 2.2 | 1.5 | 19.6 | 0.75 | 17.6 | 1.1 | 5.1 | 30.9 | 6.6 |
| Plume opacity | | Clear | Clear | Clear | Clear | Clear | Clear | | Clear | Clear | Clear | Clear |
| Plume color | | None | None | None | None | None | None | | None | Clear | None | None |

[a] $H_2$ = hydrogen; NG = natural gas.

[b] All volumes corrected to 32°F and 29.9 in. Hg.

[c] Does not include $N_2O$.

[d] Calculated on the basis that all nitrogen oxides are $NO_2$.

This gas has a distinct reddish-brown color due to its nitrogen dioxide ($NO_2$) content, but it is generally free of nitric acid mist.

## OTHER PROCESSES

Emissions from nitric acid oxidation processes, especially those used to make polymer intermediates such as adipic acid and terephthalic acid, vary widely and may, in contrast to emissions from nitric acid plants, contain high concentrations of nitrous oxide, $N_2O$ (laughing gas). In many of these processes the evolved nitrogen oxides are passed first to an absorption

TABLE 4
EMISSION AND OPERATING DATA FOR NITRIC ACID PLANTS HAVING ALKALINE SCRUBBING EQUIPMENT

| Type of control equipment | | Scrubber | | | | |
|---|---|---|---|---|---|---|
| | | NaOH & $H_2O$[a] | | $Na_2CO_3$ | | |
| Plant number | | 24 | 25 | 26 | 27 | 28 |
| Rated capacity, tons/day (100% acid basis) | | 55 | 55 | 50 | 120 | 830[c] |
| Normal acid strength, % | | 60-64 | | 54 | 56 | 40 |
| Percent of rated capacity | | 105 | 105 | 100 | 100 | 95 |
| Ammonia feed rate, lb/hr | | | | 1200 | 2900 | 23850 |
| Ammonia oxidation pressure, psig | | 110 | 110 | 60 | 110 | 13-24 |
| Absorption column exit pressure, psig | | 85 | 85 | 45 | 90 | 0 |
| Absorption column exit temp., °F | | 70 | 70 | 100 | 100 | 86 |
| Stack gas rate, Mscfm[a] | | 4.3 | 4.3 | 3.5 | 8.9 | 77 |
| Gas compositions before treatment equipment, vol. % | Oxygen | 3.8 | 4.0 | | | 3.2 |
| | Total nitrogen oxides[b] | 0.31 | 0.34 | | | 2.5 |
| | Nitogen dioxide | 0.23 | 0.18 | | | |
| | | [d] | | [d] | | |
| Gas compositions after treatment equipment, vol. % | Oxygen | | | 1.5 | | 1.5 |
| | Total nitrogen oxides | 0.03 | | 0.4 | | 0.15 |
| | Nitrogen dioxide | 0.03 | | | | |
| | Carbon dioxide | | | 1.5 | | 1.5 |
| Percent reduction in nitrogen oxides | | 91 | | | | 94 |
| Total nitrogen oxides emitted, tons/day[c] | | 0.23 | | 4.6 | | 10.7 |
| Pounds of nitrogen oxides emitted per ton of acid produced (100% basis)[c] | | 4 | | 54 | | 27 |

[a] In two stages.
[b] Does not include $N_2O$.
[c] More than one unit.
[d] Gas streams combine into one recovery device.

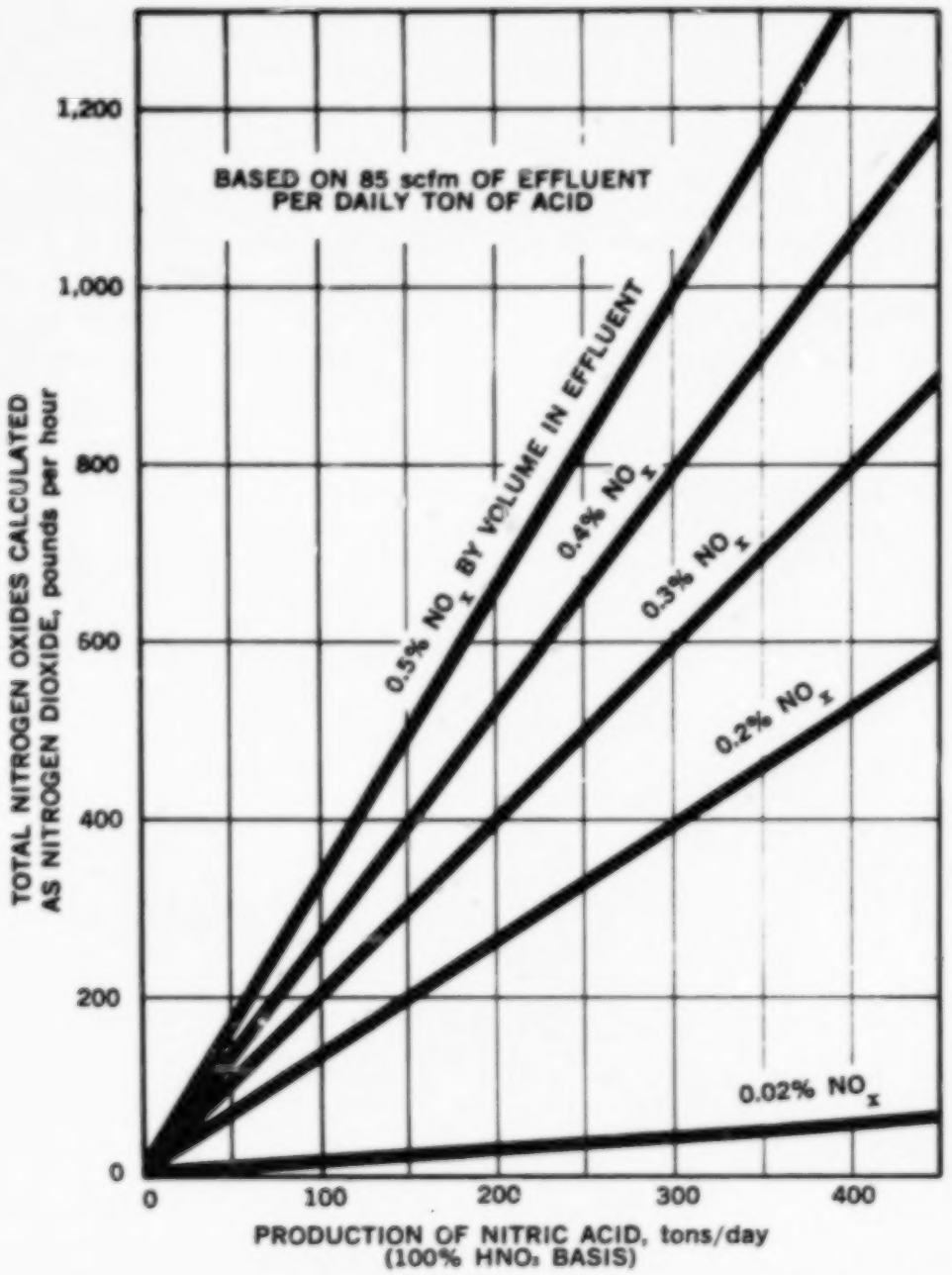


Figure 6 — Total nitrogen oxides (calculated as nitrogen dioxide) emitted per hour vs. daily production of nitric acid.

system, where a substantial portion is recovered as nitric acid. The residual gases ($N_2O$, $CO_2$, and inerts) containing small amounts of nitrogen oxides (NO and $NO_2$) are then discharged to the atmosphere. In nitration processes there is some evolution of gaseous NO and $NO_2$.

Emissions from acid storage tanks may occur during tank-filling operations. The gases displaced are equal in volume to the quantity of acid added to the tank.

Some nitrogen oxides are discharged to the atmosphere from nitric acid concentrators. The data in Table 5 show typical nitric acid feeds and compositions for a unit that produces 3,000 pounds per hour (100 percent basis) of 98 percent nitric acid.

TABLE 5

NITRIC ACID FEEDS AND COMPOSITIONS FOR A 3,000-POUND/HR (100% BASIS) NITRIC ACID CONCENTRATOR

| | Lb $HNO_3$ (100% basis) per hour |
|---|---|
| Amt of 60% acid fed to unit | 3110 |
| Amt of 98% acid produced | 3000 |
| Amt of 55% acid recovered in absorber | 90 |
| Amt of $NO_2$ vented to atmosphere (as $HNO_3$) | 20 |

The loss to the atmosphere is equivalent to 0.7 percent of the strong nitric acid produced.

The composition and quantity of gases discharged to the atmosphere are shown in Table 6 for a single nitric acid concentrator using sulfuric acid as a dehydrating agent.

TABLE 6

ATMOSPHERIC EMISSIONS FROM A 3,000-POUND/HR (100% BASIS) NITRIC ACID CONCENTRATOR

| Component | Composition, volume % | Flow Rate, lb/hr | Emissions, lb per 1000 lb of $HNO_3$ Produced |
|---|---|---|---|
| $N_2$ | 74.4 | 630 | 210 |
| $O_2$ | 20.4 | 196 | 65 |
| $NO_2$ | 1.0 | 15 | 5 |
| $H_2O$ | 4.2 | 30 | 10 |
| TOTAL | 100 | 871 | 290 |

The composition and quantity of gases emitted when the magnesium nitrate concentration system is used are essentially the same as those shown in Table 6.

Red fuming nitric acid, of interest as a rocket fuel oxidizer, is a mixture of concentrated (98 percent) nitric acid and an equilibrium mixture of nitrogen tetroxide ($N_2O_4$) and nitrogen dioxide ($NO_2$). It can be made by dissolving $N_2O_4$ in concentrated nitric acid, and is sometimes produced by total condensation of $HNO_3$ and $NO_2$ vapors, which distill from a nitric acid concentration column. Emissions associated with manufacture of red fuming nitric acid are of the same order of magnitude as those given for the production of strong nitric acid.

## PLANT OPERATING VARIABLES

Emissions of nitrogen oxides may vary widely with changes in plant operation and with faulty equipment. The main operating variables that

affect tail-gas concentrations adversely are insufficient air supply to the system, low pressure in the system (especially in the absorber), high temperatures in the cooler-condenser and absorber, the production of an excessively high-strength product acid, and operation at high through-put rates. Faulty equipment includes such items as improperly operating compressors and pumps, and leaks between rich and lean nitrogen oxide gas streams.

Insufficient air supply may be due to an undersized compressor, malfunctioning of the compressor and power-recovery equipment, or leaks in the air supply system. Oxygen is normally supplied to the system by the initial air compressor, which mixes air with ammonia before the converter and also supplies "bleach" air to the base of the absorption tower. The oxygen remaining in the gas stream leaving the ammonia converter, oxidizes the nitric oxide before the gas enters the absorption tower. Most of this oxidation occurs in the cooler-condenser system. Additional air is also heated and pumped through the product acid to remove dissolved nitrogen dioxide. This "bleach" air then enters the base of the absorption tower and is used to oxidize the nitric oxide resulting from the formation of nitric acid:

$$3NO_2 + H_2O = 2HNO_3 + NO \qquad (11)$$

Lack of oxygen will hinder the oxidation of NO to $NO_2$ and result in high nitric oxide emissions.

Routine Orsat readings will detect a lack of oxygen in the system, and corrective measures can be taken. Oxygen concentrations in the tail gas should be kept at about 3 to 4 percent oxygen.

Recent improvements in plant design include injecting additional air into the cooler-condenser to provide an increased oxygen supply. An increase in the number of plates in the absorber or in spacing of plates also provides increased oxidation time and absorption capacity, thus reducing emissions and increasing plant efficiency.

Pressure in the absorber is fixed by basic design of the unit, by compressor capacity, and by the pressure drop in the lines leading to the absorber. The rate of oxidation of nitric oxide to nitrogen dioxide increases as the square of the pressure; a small increase in absorber pressure therefore will provide a substantial increase in the rate of oxidation and indirectly in the rate of formation of nitric acid.

High temperature also causes a decrease in absorption efficiency. The rate of oxidation of nitric oxide and the rate of absorption of nitrogen dioxide vary inversely with the temperature and are favored by low temperatures. Absorption towers are cooled by circulating water in cooling coils on each plate. Temperature in the absorber is largely a function of entering gas temperature, ambient air temperature, and temperature and flow of cooling water. Cooling water throughput is dictated by pump design, and its temperature is fixed by the source of the water supply. Temperatures of the tail gas leaving the absorber normally range from 70 to 90°F.

The desire for increased acid strength often leads to higher concentrations of nitrogen oxides in the tail gas and to reduced operating efficiency. For production of stronger acid, e.g., over 60 percent, in an existing plant,

the make-up water to the absorber must be reduced and the nitrous gases passed through a stronger, more acidic solution in the absorber. The nitrogen oxides are not absorbed nearly so well in a strong acidic solution, and the emissions are thus increased. This situation cannot be corrected easily without modifying the plant structure. Increased absorber capacity, increased oxygen content, decreased temperature, and increased absorption pressure all tend to decrease tail-gas emissions while stronger acid is produced.

Leaks in process piping are easily detected and are usually repaired promptly because of the danger to operating personnel. Not so easily observed are internal leaks, which allow rich gases to leak into the lean tail gases, such as the tail-gas reheater before the final power-recovery equipment. Rich gases from the ammonia converter contain approximately 10 percent total nitrogen oxides. Only a slight leak from this stream into the tail-gas stream within the countercurrent heat exchanger will cause a definite increase in stack emission, evidenced by the darker color of the gas stream. Correction of this situation requires that the plant be shut down and the reheater section dismantled and repaired.

## SUMMARY OF SAMPLING AND ANALYTICAL TECHNIQUES

In nitric acid plants the nitrogen oxides content of the effluent streams is measured to determine the operating efficiency of the plant. In addition, oxygen concentrations are measured to check air rates to the unit. An operator usually makes these tests every 2 or 3 hours. Detailed descriptions of the methods used in the nitric acid industry to determine the oxides of nitrogen are given in Appendix A and are summarized here.

### TOTAL NITROGEN OXIDES

The hydrogen peroxide test is most commonly used in nitric acid plants to determine total nitrogen oxides. This method measures all of the various oxides of nitrogen except $N_2O$. Nitric acid mist and vapor are also measured. Although many variations are used, the technique basically involves collecting a known volume of tail gas in a glass container charged with 25 cc of 3 percent hydrogen peroxide solution. The container is sealed and allowed to react for 30 minutes, the container being shaken frequently. After 30 minutes, the container is washed with distilled water and five drops of methyl red are added. The solution is then titrated to a copper-colored endpoint with standard sodium hydroxide. The oxides are calculated as percent nitrogen dioxide. Two variations of this technique are presented in Appendix A.

This method gives accurate and reliable results in a nitric acid plant; it cannot be used in other process gas streams where interfering substances such as ammonia or sulfur dioxide are present, since they affect the acidity of the solution and the titration endpoint.

The phenoldisulfonic acid method (*13*) may also be used to determine total nitrogen oxides. The method gives comparable results, but is much more tedious. The phenoldisulfonic acid method is not subject to interference by any other compounds and thus is useful in gas streams containing ammonia, sulfur dioxide, or other interferences. It is more accurate than the peroxide method at concentrations below about 500 ppm. In the phenoldisulfonic acid method, a measured volume of tail gas is collected in a flask and reacted for approximately 24 hours with a dilute solution of sulfuric acid and hydrogen peroxide. The hydrogen peroxide oxidizes the oxides of nitrogen (with the exception of nitrous oxide) to nitric acid. The resultant solution is then neutralized and evaporated to dryness and treated with phenoldisulfonic acid reagent and ammonium hydroxide. The resulting yellow trialkali salt concentration is measured colorimetrically in a spectrophotometer at 326 $m\mu$ and the corresponding concentration of nitrogen oxides determined from a calibration curve.

If the total nitrogen oxides content of a gas stream is below 500 ppm, the Saltzman method (*14*) may prove useful and more accurate than the hydrogen peroxide method. Concentrations in this range may be encountered at the outlet of tail gas reduction equipment. This method is applicable only to gas streams containing sulfur dioxide in amounts less than the nitrogen oxide content.

## OXYGEN

A standard Orsat kit is normally used to determine the oxygen content of the tail gases. When used carefully, the kit measures oxygen concentrations to the nearest 0.2 percent by volume. The absorbing solution for oxygen is usually an alkaline pyrogallol or a chromous chloride solution. To preclude the absorption of nitrogen oxides in the oxygen-absorbing solution, the gas should first be passed through a caustic scrubber. The potassium hydroxide scrubber in the Orsat kit commonly used for $CO_2$ will serve this function.

Care must be used when sampling tail gases under high pressures. The standard Orsat kit should not be subjected to excessive pressures, since it may be damaged. A bleed off in the sample line is recommended.

## NITROGEN DIOXIDE

Nitrogen dioxide is not usually measured as a separate compound but is included in the determination of total nitrogen oxides. The measurement of nitrogen dioxide is complicated by the presence of nitric oxide, which is being constantly converted to nitrogen dioxide in the presence of oxygen. Determination of nitrogen dioxide is of interest because its photochemical reactions are important in air pollution and because the oxidation state of the tail gases affects plant operations.

Once the tail gases enter the atmosphere they are rapidly diluted, and at a concentration of 1 ppm, 70 hours are required for 50 percent conversion of NO to $NO_2$ (Figure 7). In photochemical reactions, the $NO_2$ dissociates to form NO and atomic oxygen, which in turn combines with molecular oxygen to form ozone.

The Tennessee Valley Authority has developed a method in which a solution of mixed nitric and sulfuric acids is used for determining the ratio of NO to $NO_2$. The method has been used successfully in absorption towers where the total nitrogen oxides range from 5 to 6 percent. It has shown poor reproducibility in use on tail gases.

The United States Public Health Service has developed a method for determining $NO_2$ with the Saltzman reagent. This method involves carefully diluting the tail gases by about 400:1 with nitrogen to obtain concentrations at which this reagent may be used and at which the oxidation rate is much slower.

Photoelectric instruments can be used to determine nitrogen dioxide concentrations by measuring the light absorption of the gas stream. These instruments, if carefully calibrated in the proper range, should give reliable results. An instrument procedure developed by the Du Pont Company is included in Appendix A.

## ACID MIST DETERMINATION

Acid mist is collected by drawing a measured volume of tail gas through a cyclone and a fiberglass filter. The train components are then carefully washed with distilled water and titrated with a standard base. This type



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of sampling collects only nitric acid in an actual mist form and not in the vapor state.

Stack gases are usually well above the dew point of the nitric acid mist, and no mist is present. Cooling the gas before passing it through the filter causes condensation of nitric acid present in the vapor state.

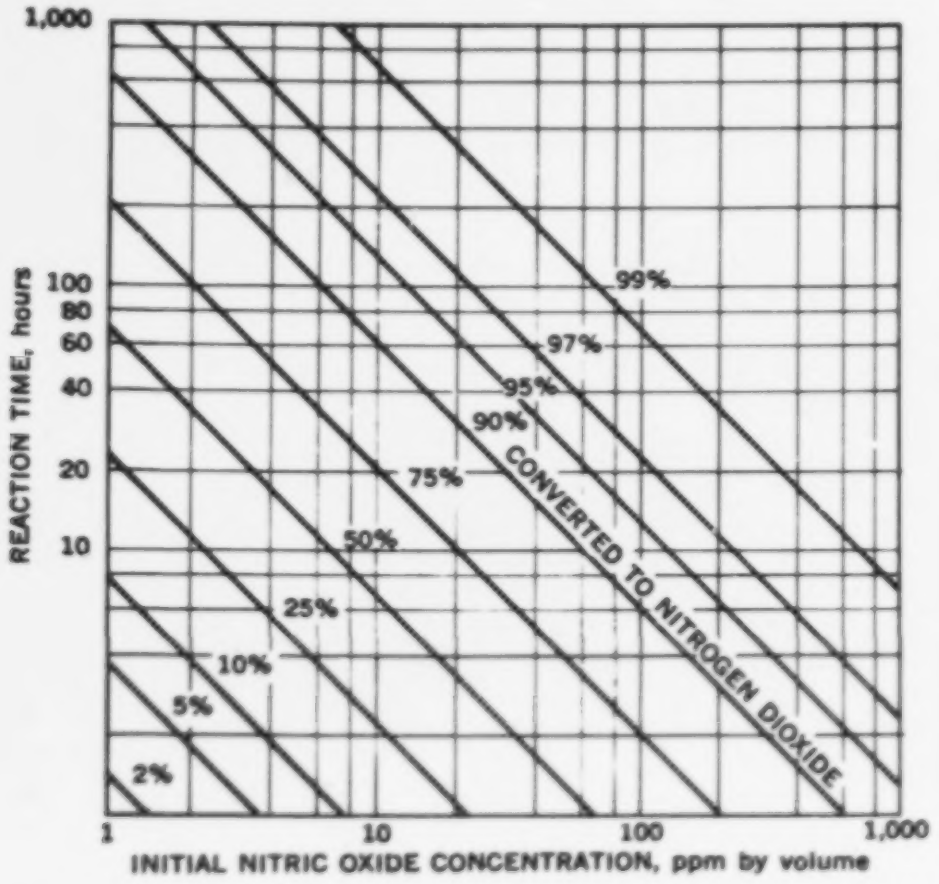


Figure 7 — Percent oxidation of nitric oxide to nitrogen dioxide by air at 25°C and 1 atmosphere.(15)

# GLOSSARY OF TERMS

*ABBREVIATIONS*

| | |
|---|---|
| °Bé | degrees Baumé |
| °C | temperature, degrees Centigrade |
| cc | cubic centimeter |
| ft | feet |
| $ft^2$ | square feet |
| $ft^3$, cf | cubic feet |
| °F | temperature, degree Fahrenheit |
| lbs | pounds |
| mg | milligram |
| mm | millimeter |
| $m_\mu$ | millimicron |
| Mscfm | thousands of standard cubic feet per minute |
| ppm | parts per million by volume |
| psig | pounds per square inch gauge |
| ® | Registered trade mark |
| scfm | cubic feet per minute measured at standard conditions: O°C (32°F) and 760 mm (29.92") Hg |
| scfh | standard cubic feet per hour |
| sp. gr. | specific gravity—compared to water at 60°F |
| °TW | degrees Twaddell |
| yr | year |

*CHEMICAL SYMBOLS*

| | |
|---|---|
| $CH_4$ | methane |
| $CO_2$ | carbon dioxide |
| Hg | mercury |
| $H_2O$ | water |
| $H_2SO_4$ | sulfuric acid |
| $HNO_3$ | nitric acid |
| NaOH | sodium hydroxide |
| $Na_2CO_3$ | sodium carbonate |
| $NH_3$ | ammonia |
| $N_2$ | nitrogen |
| $N_2O$ | nitrous oxide (laughing gas) |
| NO | nitric oxide |
| $NO_x$ | total nitrogen oxides in a mixture |
| $NO_2$ | nitrogen dioxide |
| $N_2O_4$ | nitrogen tetroxide |
| $O_2$ | oxygen |

## GLOSSARY OF TERMS (Contd.)

*DEFINITIONS*

*Absorber* — The absorber in a nitric acid plant is usually a stainless steel tower with bubble cap plates.

*Baumé (°Bé)* — Acid strength is determined by use of a floating instrument (hydrometer) calibrated to read degrees of Baumé and by a conversion chart. The Baumé can also be calculated if the specific gravity of the acid at 60°F is known:

$$°Bé = 145 - \left(\frac{145}{\text{sp. gr.}}\right)$$

*Catalyst* — In a nitric acid plant "catalyst" usually refers to the platinum-rhodium woven wire gauze on which the ammonia is oxidized to nitric oxide and water.

*Catalytic reduction system* — A device for reducing the emissions of nitrogen oxides to the atmosphere by passing the gas over a catalyst in the presence of a reducing fuel such as natural gas, hydrogen or ammonia.

*Converter* — The chamber in which the ammonia is converted to nitric oxide and water by reacting it with air over a platinum-rhodium catalyst.

*Effluent* — Waste gas stream that enters the atmosphere from the process.

*Emission* — Any gas stream emitted to the atmosphere.

*Establishment* — A works having one or more nitric acid plants or units, each being a complete production entity.

*Fuming nitric acid* — A mixture of 98 percent nitric acid and an equilibrium mixture of nitrogen tetroxide ($N_2O_4$) and nitrogen dioxide ($NO_2$).

*Nitric acid mist* — Extremely small particles of acid in the liquid state.

*Nitric acid (strong)* — Concentrated 98 percent nitric acid.

*Nitric acid vapor* — Nitric acid in the gaseous state.

*Nitric acid (weak)* — 55 to 65 percent nitric acid.

*Nitrogen oxides* — A general term pertaining to a mixture of nitric oxide (NO) and nitrogen dioxide ($NO_2$).

*Tail gas* — The gas leaving the nitric acid absorber.

*Twaddell (°TW)* — A measure of acid density and strength.

$$°TW = \frac{\text{sp. gr.} - 1}{0.005}$$

## APPENDICES


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# APPENDIX A: SAMPLING AND ANALYTICAL TECHNIQUES

The sampling and analytical techniques described here were used to obtain the emission data presented in this report and are those generally used in the nitric acid manufacturing industry. Format and wording for most of these procedures are those of the company that supplied the description.

# NITRIC OXIDE (NO) PLUS NITROGEN DIOXIDE ($NO_2$) IN GAS SAMPLES — MODIFIED GAILLARD METHOD — E. I. duPONT de NEMOURS AND COMPANY

## PRINCIPLE AND STATUS

This method determines NO plus $NO_2$ in a gas sample of known volume by converting the oxides of nitrogen to nitric acid with excess aqueous hydrogen peroxide and titrating the acid with standard sodium hydroxide.

Equations for the reactions with peroxide may be written:

$$2NO_2 + H_2O_2 \rightarrow 2HNO_3$$
$$2NO + 3H_2O_2 \rightarrow 2HNO_3 + 2H_2O$$

The method does not differentiate between NO and $NO_2$. Any $N_2O_4$ that may be present is counted as $NO_2$. $N_2O$ does not interfere.

A trace of cupric sulfate is added to the hydrogen peroxide to increase the rate of absorption of NO. Cupric sulfate catalyzes decomposition of peroxide; the liberated oxygen reacts with NO to form $NO_2$, which is absorbed more rapidly than NO.

Because accurate measurement of sample volume is necessary, the method is not applicable to gases that contain significant amounts of condensed liquids such as water or nitrogen tetroxide. It is applicable to product gas from an NO generator, sampled downstream from the cooler condenser, and to other gas samples containing no condensed phase.

Standard deviation (95% confidence level) is ± 0.12 percent at the 20 percent NO level based on 30 determinations by one analyst over a period of one week.

## SAFETY PRECAUTIONS

Wear rubber gloves and an apron when handling 30 percent hydrogen peroxide, avoiding all contact with the skin and inhalation of vapor. If the peroxide contacts the skin, flush immediately with large amounts of water to prevent severe burns. Open new bottles carefully behind a shield in a hood. Store in a cool area away from alkalies, ammonia, and chlorides; ferrous, mercurous, or gold salts, hypophosphites, iodides, permanganates, sulfites; and organic matter in general.

The maximum allowable concentration of $NO_2$ in air is 5 ppm. The greatest hazard of exposure to $NO_2$ is that its serious effects are not felt until several hours after exposure and that dangerous amounts may be inhaled before any real discomfort occurs. NO is an extremely toxic gas, which is rapidly converted to $NO_2$ by the oxygen of the air.

## NO PLUS $NO_2$

### Apparatus and Reagents

*Gas sampling bulb*—300-500 ml, Corning Glass Co., Cat. No. 9500 or equivalent.

*Thermometers*:

EL-2 -5° to +25°C, Specification 1009.

EL-3, +20° to +50°C, Specification 1010.

*30-ml syringe.*

*3 percent Hydrogen peroxide*—Dilute 50 ml of 30 percent $H_2O_2$ to 500 ml with distilled water. One ml of this solution is equivalent to about 0.6 millimoles of NO. Three percent $H_2O_2$ designated "U.S.P." is not suitable because it contains acetanilide, which interferes with the end point.

*Methyl Purple® indicator*—Fisher Scientific Co., Cat. No. So-I-9.

*0.1N standard sodium hydroxide.*

*Kel-F® stopcock grease.*

*1 percent Copper sulfate solution*—Dissolve 1 g of reagent grade anhydrous CuSO4 in 100 ml of distilled water.

**Calibration of Gas Sampling Bulbs**

Care in cleaning and lubricating gas sampling bulbs is essential for precise analytical results. Clean new bulbs with chromic acid cleaning solution. Use Kel-F® to lubricate the stopcocks. Never use silicone grease, because it coats the interior walls of the bulb and interferes with proper drainage. Bulbs contaminated with silicone grease may be cleaned with hot 5 percent sodium hydroxide solution.

Weigh the clean, dry bulb to the nearest 0.01 gram.

Fill the bulb with water so the bore of one stopcock contains water. Use a pipe cleaner to remove water remaining in the stopcock stem. Record the temperature of the water and reweigh the bulb to the nearest 0.01 gram.

**Calculation:**

$$\text{Capacity of bulb at t°C, ml} = \frac{A - B}{d_t - 0.0010}$$

where $A$ = weight of bulb plus water, grams

$B$ = weight of bulb, grams

$d_t$ = density of water at observed temperature, t°C.

0.0010 = buoyancy constant, grams per ml

**Analysis of Samples**

Rinse a gas-sampling bulb with distilled water and dry in a stream of clean air. If the water does not wet the bulb evenly, or if the water drains, leaving droplets adhering to the walls, clean the bulb with chromic acid cleaning solution. Check the bulb again for cleanliness before using.

Connect a clean, dry gas-sampling bulb to the source of gas to be analyzed and purge for 5 to 10 minutes at a flow rate of at least 1 liter per minute.

Reduce the flow rate and pressurize the sample slightly by closing the

outlet stopcock first, then the inlet stopcock. If there is a regulator on the sample source, adjust to about 2 psig before closing the stopcocks.

Place the sample bulb in an area not subject to large temperature variations and allow to stand for 30 minutes to reach room temperature. Open one stopcock for about 1 second to equilibrate with atmospheric pressure.

Repeat previous step. Record the room temperature to the nearest 0.1°C and atmospheric pressure to the nearest 0.1 mm.

Add one drop of 1 percent CuSO4 to 30 ml of 3 percent $H_2O_2$ in a 50-ml beaker. Since CuSO4 acts as a decomposition catalyst for $H_2O_2$, do not prepare this solution until ready to use.

Attach a 3-inch length of rubber tubing to a 30-ml syringe and draw 25 ml of the $CuSO_4$-$H_2O_2$ solution into the syringe. Attach the other end of the rubber tubing to the stopcock stem at one end of the sample bulb, apply gentle pressure, and open the stopcock just long enough to admit the solution.

Allow the bulb to stand 1 hour with occasional vigorous shaking to complete the oxidation and absorption of nitrogen oxides. This period may be shortened by placing the sample bulb on an automatic shaker and shaking continuously. If the red-brown color of $NO_2$ persists after 1 hour, indicating incomplete absorption, repeat the period of standing and shaking.

If no $NO_2$ is visible, wash the contents of the bulb into a 250-ml beaker with about 100 ml of distilled water. This may conveniently be done by holding the bulb in a vertical position, opening both stopcocks, and inserting the tip of a wash bottle into the stem of the upper stopcock while rinsing.

Titrate with 0.1N NaOH to a Methyl Purple® end point. When a new bottle of 30 percent $H_2O_2$ is opened, determine a blank to make certain the $H_2O_2$ is not acidic enough to interfere with the analysis. Normally, correction for a blank is not necessary.

**Calculation:**

$$\text{Mole percent total } (NO + NO_2) = \frac{\text{ml NaOH x normality x } V_m \text{ x } 100}{\text{volume of sample bulb, ml}}$$

$$\text{where } V_m = (22.414)\left(\frac{760}{P}\right)\left(\frac{273.2 + t}{273.2}\right) = (62.35)\left(\frac{273.2 + t}{P}\right)$$

t = room temperature, °C

P = pressure, mm Hg, at the time of the final pressure equilibration.

Clean the sample bulb with acetone and lubricate the stopcocks with Kel-F® after each analysis.

# DETERMINATION OF OXIDES OF NITROGEN AS NITRATE — HYDROGEN PEROXIDE METHOD — PUBLIC HEALTH SERVICE

## SCOPE

This method comprises a nonspecific test for the oxides of nitrogen (with the exception of $N_2O$) and is easily completed in the field. It actually determines total acidity of the gas stream; precautions must be taken in interpreting the results since many other compounds may interfere if present in the gas stream. These include $SO_2$, $SO_3$, and $NH_3$. Results are reported as ppm $NO_2$ by volume.

## APPARATUS (Figures A1 and A2)

*Sampling probe*—Stainless steel (type 304 or 316) or glass tubing of suitable size (¼-inch-OD, 6-foot-long stainless steel tubing has been used).

*Collection flask*—A clean 2-liter round-bottom flask with an outer 24/40 joint for integrated samples or a 250-ml sampling tube for grab samples.

*Adapter with stopcock*—Adapter for connecting collection flask to sampling "T".

*Three-way stopcock.*

*Manometer*—A 36-inch Hg manometer.

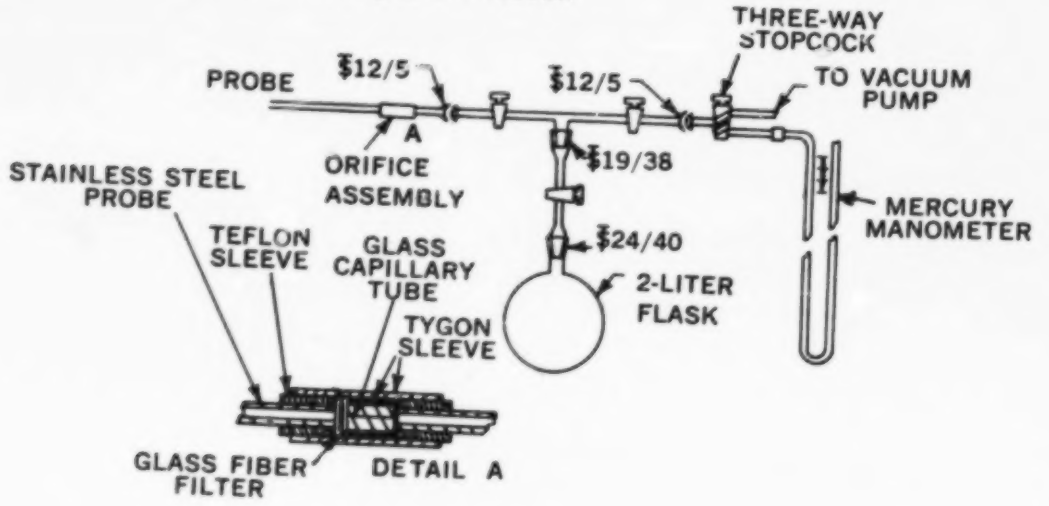


Figure A1 — Apparatus for integrated grab samples.

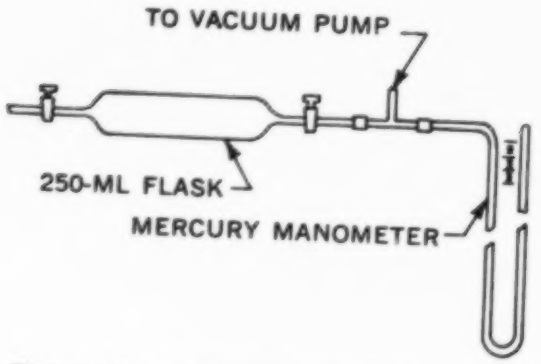


Figure A2 — Apparatus for grab samples.

## APPENDIX A

## REAGENTS

*30 Percent hydrogen peroxide* (reagent grade).

*3 Percent hydrogen peroxide*—Dilute 30 percent $H_2O_2$ with distilled water at 10:1 ratio. Prepare fresh daily.

*0.01 sodium hydroxide*—Dissolve 40 grams NaOH in 40 grams $H_20$. Decant the clear solution and dilute about 2000:1. Standardize against potassium acid phthalate or similar reagent.

*0.1 Percent Methyl Red Indicator.*

## SAMPLING PROCEDURE

Add 25 ml of freshly prepared 3 percent hydrogen peroxide solution to the sampling flask. Evacuate the sample flask, record pressure in flask. Record all values on data sheet, shown in Figure A3. Purge the sample line for about 1 minute. With probe valve still open, hold probe directly in the gas stream and open flask stopcock. When flask has reached approximately 90 percent of atmospheric pressure, close stopcock and record final vacuum in flask.

## SAMPLE PREPARATION

Shake flask thoroughly every 10 minutes for ½ hour and then set aside for an additional ½ hour.

## ANALYTICAL PROCEDURE

Remove sample line and wash the region between the stopcock and joint with distilled water, catching the washings in the sample flask. Wash the joint and flask walls with a jet of distilled water. Add 5 drops of 0.1 percent methyl red indicator and titrate with standardized 0.01N NaOH to a copper-colored endpoint. A blank should be run simultaneously.

## CALCULATION

$$\text{ppm } NO_2 \text{ by volume} = \frac{(\text{ml NaOH}) \times (\text{N NaOH}) \times 24.1 \times 10^6}{V_a}$$

$$\text{where: } V_a = (V_n - V_r)\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) \times \frac{530°R}{29.9" \text{ Hg}}$$

$V_r$ = volume of reagent, ml

$V_n$ = volume of flask at 70°F and 29.9 in. Hg, ml

$P_i$ = absolute pressure in flask after evacuating, in. Hg

$P_f$ = final absolute pressure in flask after sampling, in. Hg

$T_i$ = initial temperature in flask, °R.

$T_f$ = final temperature in flask, °R.

DATE_____ TEST NO._____ LOCATION_____

Type of Operation_____

Sampling Flask No._____ Flask Volume, Vo _____ ml

Volume of Reagent, $V_r$ _____ml

Barometric Pressure, $P_b$= _____in. Hg

Initial Flask Vacuum, $P_1$

leg 1 _____
leg 2 _____
_____

$P_1$=_____ in. Hg

$P_i = P_b - P_1$ = _____

Final Flask Vacuum, $P_2$

leg 1 _____
leg 2 _____
_____

$P_2$=_____in. Hg

$P_f = P_b - P_2$ = _____

Initial Flask Temperature_____ $^{o}F$ + 460 =_____ $^{o}R$

Final Flask Temperature_____ $^{o}F$ + 460 =_____ $^{o}R$

---

CALCULATIONS:

$$ppm\ NO_x = \frac{(ml\ NaOH) \times (N\ NaOH) \times 24.1 \times 10^6}{V_s\ (ml)}$$

$$V_s = (V_o - V_r)\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right)(17.7)$$

Titrations - final reading_____ Normality of NaOH_____

initial reading_____

Total titration _____ml

Figure A3 — Data sheet for field evaluation of total nitrogen oxides by hydrogen peroxide method.

# PHENOLDISULFONIC ACID METHOD FOR TOTAL NITROGEN OXIDES — PUBLIC HEALTH SERVICE

## SCOPE

When sulfur dioxide, ammonia, or other compounds that interfere with the hydrogen peroxide method are present in the gas to be sampled and/or the concentration of the nitrogen oxides is below about 100 ppm, this method is used. Accuracy below 5 ppm is questionable. This test is unsuitable for atmospheric sampling.

## APPARATUS (Figures A1 and A2)

*Sampling probe*—Stainless steel (type 304 or 316) or glass tubing of suitable size (¼-inch-OD, 6-foot-long stainless steel tubing has been used).

*Collection flask*—A 2-liter round-bottom flask with an outer 24/40 joint for integrated samples or a 250-ml MSA sampling tube for grab samples.

*Orifice assembly*—The size of the glass capillary tubing depends on the desired sampling period (flow rates of about 1 liter per minute have been used). Use of this orifice is not mandatory.

*Adapter with stopcock*—Adapter for connecting collection flask to sampling "T".

*Three-way stopcock.*

*Manometer*—A 36-inch Hg manometer or accurate vacuum gage.

*Spectrophotometer*—Beckman Model "B" or equivalent.

## REAGENTS

*30 Percent hydrogen peroxide*—(reagent grade).

*3 Percent hydrogen peroxide*—Dilute 30 percent $H_2O_2$ with water at 1:10 ratio. Prepare fresh daily.

*Concentrated Sulfuric Acid.*

*0.1N (approximate) Sulfuric Acid*—Dilute 2.8 ml concentrated $H_2SO_4$ to 1 liter with water.

*Absorbing Solution*—Add 12 drops 3 percent $H_2O_2$ to each 100 ml 0.1N $H_2SO_4$. Make enough for required number of tests.

*1N (approximate) sodium hydroxide*—Dissolve 40 gm NaOH pellets in water and dilute to 1 liter.

*Concentrated ammonium hydroxide.*

*Fuming sulfuric acid*—15 to 18 weight percent free sulfuric anhydride (oleum).

*Phenol* (reagent grade)

*Phenoldisulfonic acid solution*—Dissolve 25 grams of pure white phenol

in 150 ml concentrated $H_2SO_4$ on a steam bath. Cool and add 75 ml fuming sulfuric acid. Heat to 100°C for 2 hours. Store in a dark stoppered bottle. This solution should be colorless if prepared with quality reagents.

*Potassium nitrate* (reagent grade).

*Standard potassium nitrate solution*—Solution A: Dissolve 0.5495 gram $KNO_3$ and dilute to 1 liter in a volumetric flask. Solution B: Dilute 100 ml of Solution A to 1 liter. One ml of Solution A contains the equivalent of 0.250 mg $NO_2$ and of Solution B, 0.0250 mg $NO_2$.

## CALIBRATION

Calibration curves are made to cover different ranges of concentrations. Using a microburette for the first two lower ranges and a 50-ml burette for the next two higher ranges, transfer the following into separate 150-ml beakers (or 200-ml casseroles).

1. 0-100 ppm: 0.0 (blank), 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 16,0, 20.0 ml of $KNO_3$ Solution B.
2. 50-500 ppm: 0.0 (blank), 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0 ml of $KNO_3$ Solution A.
3. 500-1500 ppm: 0.0 (blank), 5.0, 10.0, 15.0, 20.0, 25.0, 30.0 ml of $KNO_3$ Solution A.
4. 1500-3000 ppm: 0.0 (blank), 15.0, 30.0, 35.0, 40.0, 45.0, 50.0, 55.0, 60.0 ml $KNO_3$ Solution A.

Add 25.0 ml absorbing solution to each beaker. Follow as directed in the Analytical Procedure section starting with the addition of 1N NaOH.

After the yellow color has developed, make dilutions for the following ranges: 50 to 500 ppm (1:10); 500 to 1500 ppm (1:20); and 1500 to 3000 ppm (1:50). Read the absorbance of each solution at 420m$_\mu$.

Plot concentrations against absorbance on rectangular graph paper. A new calibration curve should be made with each new batch of phenoldisulfonic acid solution or every few weeks.

## SAMPLING PROCEDURE

*Integrated Grab Sample*—Add 25 ml freshly prepared absorbing solution into the flask. Record the exact volume of absorbing solution used.

Set up the apparatus as shown in Figure A1, attach the selected orifice. Purge the probe and orifice assembly with the gas to be tested before sampling begins by applying suction to it. Evacuate the system to the vapor pressure of the solution: this pressure is reached when the solution begins to boil. Record the pressure in the flask and the ambient temperature. Open the valve to the sampling probe to collect the sample. Constant flow will be maintained until the pressure reaches 0.53 of the atmospheric pressure. Stop before this point is reached. During sampling, check the rate of fall of the mercury in one leg of the manometer in case clogging, especially of the

orifice, occurs. At the end of the sampling period, record the pressure, temperature, and barometric pressure.

An extended period of sampling can be obtained by following this procedure. Open the valve only a few seconds at regular intervals. For example: Open the valve for 10 seconds and close it for 50 seconds; repeat every 60 seconds.

*Grab Sample*—Set up the apparatus as shown in Figure A2 for high concentrations (200-3000 ppm) or the apparatus as shown in Figure A1 for low concentrations (0-200 ppm) but delete the orifice assembly. The same procedure is followed as in the integrated method except that the valve is opened at the source for about 10 seconds and no orifice is used.

## SAMPLE PREPARATION

Shake the flask for 15 minutes and allow to stand overnight.

## ANALYTICAL PROCEDURE

Transfer the contents of the collection flask to a beaker. Wash the flask three-times with 15-ml portions of $H_2O$ and add the washings to the solution in the beaker. For a blank add 25 ml absorbing solution and 45 ml $H_2O$ to a beaker. Proceed as follows for the blank and samples.

Add 1N NaOH to the beaker until the solution is just alkaline to litmus paper. Evaporate the solution to dryness on a water bath and allow to cool. Carefully add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a glass rod, making sure that all the residue comes into contact with the solution. Add 1 ml $H_2O$ and four drops concentrated $H_2SO_4$. Heat the solution on the water bath for 3 minutes, stirring occasionally.

Allow to cool and add 20 ml $H_2O$, mix well by stirring, and add 10 ml concentrated $NH_4OH$, dropwise, stirring constantly. Transfer the solution to a 50-ml volumetric flask, washing the beaker three times with 4- to 5-ml portions of $H_2O$. Dilute to mark with water and mix thoroughly. Transfer a portion of the solution to a dry, clean centrifuge tube and centrifuge, or filter a portion of the solution.

Read the absorbance of each sample at 420 $m_\mu$. If the absorbance is higher than 0.6, make a suitable dilution of both the sample and blank and read the absorbance again.

## CALCULATIONS

$$\text{ppm } NO_2 = \frac{(5.24 \times 10^5)\ (C)}{V_s}$$

Where $C$ = concentration of $NO_2$, mg (from caiibration chart)

$V_s$ = gas sample volume at 70°F and 29.92 in Hg, ml.

# NITROGEN DIOXIDE OR TOTAL NITROGEN OXIDES DETERMINATION WITH GRIESS-SALTZMAN REAGENT — PUBLIC HEALTH SERVICE

## SCOPE

The technique employed for determination of nitrogen dioxide and of total nitrogen oxides when concentrations are below 500 ppm is colorimetric analysis with Griess-Saltzman reagent. This method is acceptable for nitric acid plants or other sources where the interference of sulfur dioxide is not encountered.

## APPARATUS

*Sampling Probe*—Stainless steel (304 or 316) or glass tubing with sampling tee (¼-inch-OD tubing has been used).

*Self-sealing serum cap*—Rubber. (A serum cap with 11/32-inch sleeve and 7/32-inch plug has been used. Chemical Rubber Company, Catalog No. 13-8855).

*Gas syringe*—5 ml, gas tight, with Teflon plunger and/or 100-ml glass syringe (needle should be about No. 22).

*Collection flask*—A 2-liter glass flask for nitrogen dioxide and a 250-ml gas-sampling tube for total oxides.

*Flask adaptor*—Any suitable fitting to reduce the 2-liter flask opening to the size of the serum cap available.

*Spectrophotometer*—Beckman Model "B" or equivalent.

*Thermometer*—For ambient temperature.

*Barometer*—Barometric pressure, in. Hg.

## REAGENTS

*Nitrogen supply*—Cylinder nitrogen with low oxygen content.

*Glacial acetic acid.*

*Sulfanilic acid.*

*N-(1-Naphthyl)-ethylenediamine dihydrochloride.*

*Absorbing solution*—To 6 liters of distilled water, add 1120 ml glacial acetic acid, 40 gm sulfanilic acid, and 0.160 gm N-(1-Naphthyl)-ethylenediamine dihydrochloride. Dilute to 8 liters with water and store in a dark bottle at about 45°F.

*Sodium nitrite*—(reagent grade).

*Standard sodium nitrite solution*—Accurately weigh 2.03 gm $NaNO_2$ and dissolve in water. Dilute to 1 liter. Transfer 10 ml of this solution to a 1-liter volumetric flask and dilute to 1 liter. One ml of this standard solution

is equivalent to 10 $\mu$l $NO_2$ at 25°C and 760 mm Hg. It has been shown empirically that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide.*

## CALIBRATION

Transfer 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 ml respectively of the dilute standard sodium nitrite solution to six 25-ml volumetric flasks and fill the flasks to the mark with absorbing solution. Shake thoroughly and allow 15 minutes for color development. Read the absorbance at 550 m$\mu$ in a spectrophotometer using fresh absorbing solution as a blank. Plot concentrations against absorbances on rectangular graph paper.

Make a new calibration curve for each new batch of absorbing solution.

## SAMPLING PROCEDURE

*Nitrogen dioxide*—Add 50 ml of absorbing solution to a dry 2-liter flask. Purge the flask and adapter with nitrogen and immediately seal with a serum cap.

Insert the gas tight syringe through a serum cap in the sampling tee and flush the syringe several times with sample gas. Draw into the syringe exactly 5 ml of sample gas and quickly inject the sample into the 2-liter flask. Allow the sample to absorb for 15 minutes, shaking several times during this period.

After 15 minutes, drain the absorbing solution into a sealed container (e.g. a 50-ml volumetric flask) and allow to stand 15 minutes longer for color development (the transfer need not be quantitative).

*Nitrogen oxides* (1) syringe method—Fill a 100-ml glass syringe with absorbing solution. Adjust to 90 to 100 ml, taking care to expel all air bubbles. Cap the needle to prevent leakage of solution.

To sample, expel enough solution to reach the 80-ml mark and insert the needle into the sampling tee. Carefully retract the plunger to the 100-ml mark and then withdraw it from the sample line. Seal the needle tip with a rubber stopper and place the syringe in a dark location for 24 hours.

(2) Gas Sample Tube—Fill a 250-ml gas tube with absorbing solution, eliminating all air. Connect one end of the tube to the sample probe with a short piece of Tygon tubing and insert the other end into a 110-ml volumetric flask. (100 ml + 10 ml graduated neck). Open the bottom stopcock and by manipulating the top stopcock, drain 100± ml of reagent into the volumetric flask. Close the bottom stopcock and set the tube in a dark location for 24 hours. (The 100+ ml should be drained quite rapidly and care taken not to agitate the absorbing solution. These steps minimize absorption during the sampling period).

---

*Molar volume at 25°C and 760 mm Hg is 24.47 liters therefore:

$$2.03 \times 10^{-5}\text{gm} \times \frac{1}{69.0} \times \frac{1}{0.72} \times 24.47 = 10 \times 10^{-6}\ \text{l}\ NO_2 = 10\ \mu\text{l}\ NO_2$$

In all cases, record the barometric pressure (in. Hg) and ambient temperature (°F).

## ANALYTICAL PROCEDURE

After the specified waiting period has elapsed, shake the containers well. Transfer the absorbing solution to 1 cm cells and measure the absorbance at 550 $m\mu$ against unused absorbing solution as a reference. Dilutions with fresh absorbing solution may be made if necessary.

## CALCULATIONS

$$\text{ppm } NO_2 = \frac{(C)\ (V_r)\ (1000)}{(V_s)}$$

$C$ = concentration of $NO_2$ from calibration graph ($\mu$l $NO_2$/ml reagent).

$V_r$ = volume of reagent, ml

for nitrogen dioxide = 50 ml

for syringe = 80 ml

for gas tube, volume of tube minus reagent withdrawn

$V_s$ = sample volume at 29.92 in. Hg and 25°C.

$$= V\left(\frac{P_b}{29.92}\right)\left(\frac{298}{273+T_a}\right)$$

$V$ = sample taken, ml

for nitrogen dioxide — 5 ml

for syringe — 20 ml

for gas tube, volume of reagent withdrawn

$P_b$ = barometric pressure, in. Hg.

$T_a$ = ambient temperature, °C.

# NITROGEN DIOXIDE — DETERMINATION IN GAS STREAMS BY USE OF THE MODEL 4 PHOTOELECTRIC ANALYZER
# E. I. duPONT de NEMOURS AND COMPANY

## PRINCIPLE AND STATUS

Nitrogen dioxide ($NO_2$), a red-brown gas, dimerizes very rapidly and reversibly to form colorless nitrogen tetroxide ($N_2O_4$) according to the reaction:

$$2NO_2 \rightleftarrows N_2O_4$$

At ordinary temperatures both $NO_2$ and $N_2O_4$ are always present in equilibrium in the gas. A photometric measurement of the color intensity of $NO_2$ provides a rapid, continuous method for determining only $NO_2$ without affecting the $NO_2$-$N_2O_4$ equilibrium. The wet chemical method uses peroxide to oxidize the nitrogen (IV)* oxides to nitric acid followed by titration with a standard base. This method does not distinguish between $NO_2$ and $N_2O_4$, but gives total nitrogen (IV)* oxides calculated as mole percent $NO_2$, which is equivalent to mole percent $NO_2$ plus twice mole percent $N_2O_4$.

$NO_2$ absorbs light strongly between 400 m$\mu$ and 600 m$\mu$, while the other nitrogen oxides do not absorb in this region of the spectrum. The Model 4 Photoelectric Analyzer, at an analyzing wavelength of 436 m$\mu$ and a reference wavelength of 546 m$\mu$, is used to determine $NO_2$ in gas streams containing $N_2O$, NO, $N_2O_4$, $HNO_3$, $N_2$, $O_2$, $CO_2$, and water vapor. The full-scale range of the instrument with a 10-cm cell is from 1500 ppm $NO_2$ to 2.0 mole percent $NO_2$. This method is not recommended for concentrations of $NO_2$ greater than 2 mole percent. The Model 4 Photoelectric Analyzer can be used to determine concentrations of $NO_2$ greater than 2 mole percent by changing the wavelengths and using a heated cell.

## SAFETY PRECAUTIONS

Conduct all work in a well-ventilated area, venting the sample stream in a hood or into an exhaust system.

NO and $NO_2$ are extremely toxic gases. The maximum allowable concentration of $NO_2$ in air is 5 ppm. Exposure to 100 ppm NO or $NO_2$ for 30 to 60 minutes is dangerous. The greatest hazard of exposure to $NO_2$ is that its serious effects are not felt until several hours after exposure and that dangerous amounts may be inhaled before any real discomfort occurs.

*Valence of 4.

## $NO_2$

## APPARATUS AND REAGENTS

Model 4 Photoelectric Analyzer, Manufacturers Engineering and Equipment Corporation, Hatboro, Pa., or Du Pont 400 Photometric Analyzer, Instrument Products Division, Wilmington, Del., equipped with the following optical filters:

Measuring Beam—436 $m_\mu$

2 pieces Corning CS 3-73 (3389) Du Pont 400-340-6

1 piece Corning CS 5-58 (5113) Du Pont 400-340-8

Reference Beam—546 $m_\mu$

1 piece Corning CS 3-69 (3486) Du Pont 400-340-7

1 piece Corning CS-1-60 (5120) Du Pont 400-340-9

Beam Splitter—50% Transmission Du Pont 400-330-3

Calibration Filter—Corning CS 3-75 (3060)

1 piece 0.23-0.26% $NO_2$ for 10 cm cell

2 pieces 0.45-0.50% $NO_2$ for 10 cm cell

Sampling system, Figure A4. Stainless steel needle valves should be used. All lines should be made of stainless steel, glass, and/or Teflon. All connectors should be stainless steel or Teflon. Beckman Teflon tube fittings are excellent in this application. Rubber and Tygon connections should be avoided. Keep sample lines as short as possible.

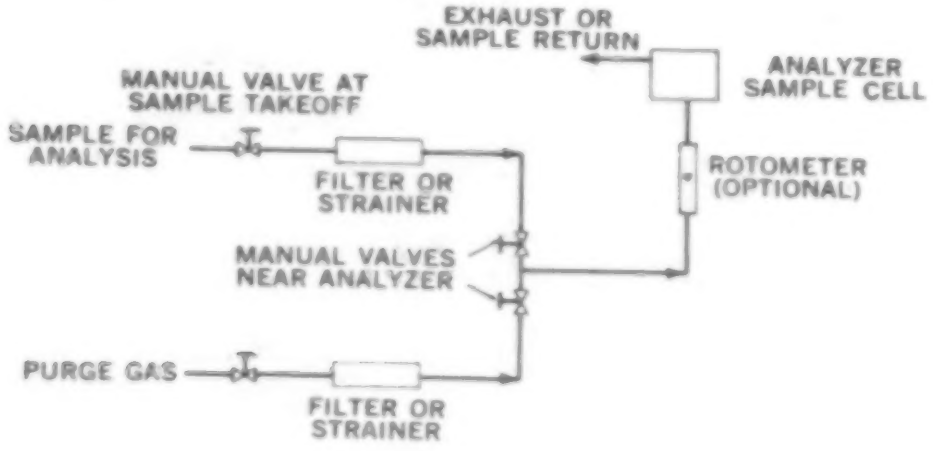


Figure A4 — Sampling system for model 4 photoelectric analyzer.

Rotameter, Tru-Taper Tube, sizes 2-15-3 with stainless steel float, range 160-1600 ml/min., Brooks Rotameter Co., Lansdale, Pa.

Gas sampling bulb, 300-500 ml, Corning Glass Co., Cat. No. 9500 or equivalent.

$NO_2$ standard gas mixture. Mixtures of $NO_2$ and $N_2$ containing 0-2 percent $NO_2$ can be obtained from Matheson Co., Inc., P. O. Box 85, East Rutherford, N. J. Determine total nitrogen (IV) oxides as mole percent $NO_2$ in these mixtures by the modified Gaillard procedure.

## ZERO ADJUSTMENT OF MODEL 4 ANALYZER

Purge the sample lines and cell with a dry, colorless gas (e.g. instrument air, nitrogen, clean laboratory air).

Make certain the calibration filter is *not* in the light path.

Adjust the COARSE ZERO and FINE ZERO controls until the recorder

reads zero. Turn the COARSE ZERO and the FINE ZERO knobs clockwise to move the recorder pen upscale and counterclockwise to move the pen downscale.

If the instrument cannot be zeroed consult the operating manual. Probable trouble sources are a dirty sample cell, weak batteries, an open signal cable, gassy phototubes, broken optical filters, or defective amplifier tubes. Major repairs and adjustments should be undertaken only by qualified instrument shop personnel.

**SPAN ADJUSTMENT**

Purge the sample cell with a dry, colorless gas (e.g. instrument air, nitrogen, clean laboratory air).

Make certain the calibration filter is *not* in the light path.

Check the instrument zero. If the zero has shifted, repeat zero adjustment.

Insert the calibration filter in the light path by pulling up the calibration filter knob.

Adjust the SPAN control to give the desired recorder deflection for the calibration filter being used. For example, to set the analyzer to read 2.0 mole percent $NO_2$ full scale, use a 10 cm cell and a calibration filter made of two pieces of Corning glass CS 3-75 (3060) having an equivalent $NO_2$ value of 0.50 percent; adjust the SPAN control to give a recorder deflection of 25 percent of full scale.

Recheck the zero setting after SPAN adjustment because a change in the SPAN control may cause a shift in zero. Except for purging, the span adjustment may have to be repeated several times before zero and span settings are correct and stable.

**DETERMINATION OF $NO_2$**

Purge the sample cell as before.

Zero the analyzer.

Make span adjustment.

Pass the gas stream to be analyzed through the sample cell, adjusting the flow rate to not less than 500 ml/min for a 10 cm cell. This minimum flow rate insures negligible photodecomposition of the $NO_2$ which causes low results.

Read from the recorder chart the concentration of $NO_2$ in the sample.

From Figure A5, determine total nitrogen (IV) oxides as mole percent $NO_2$ corresponding to the mole percent $NO_2$ read on the analyzer recorder chart. Figure A5 shows curves for three different temperatures. Select the curve closest to the temperature of the sample cell. For example, the analyzer indicates a gas stream contains 1.50 mole percent $NO_2$ at 35°C; total nitrogen (IV) oxides as mole percent $NO_2$ is 1.64.

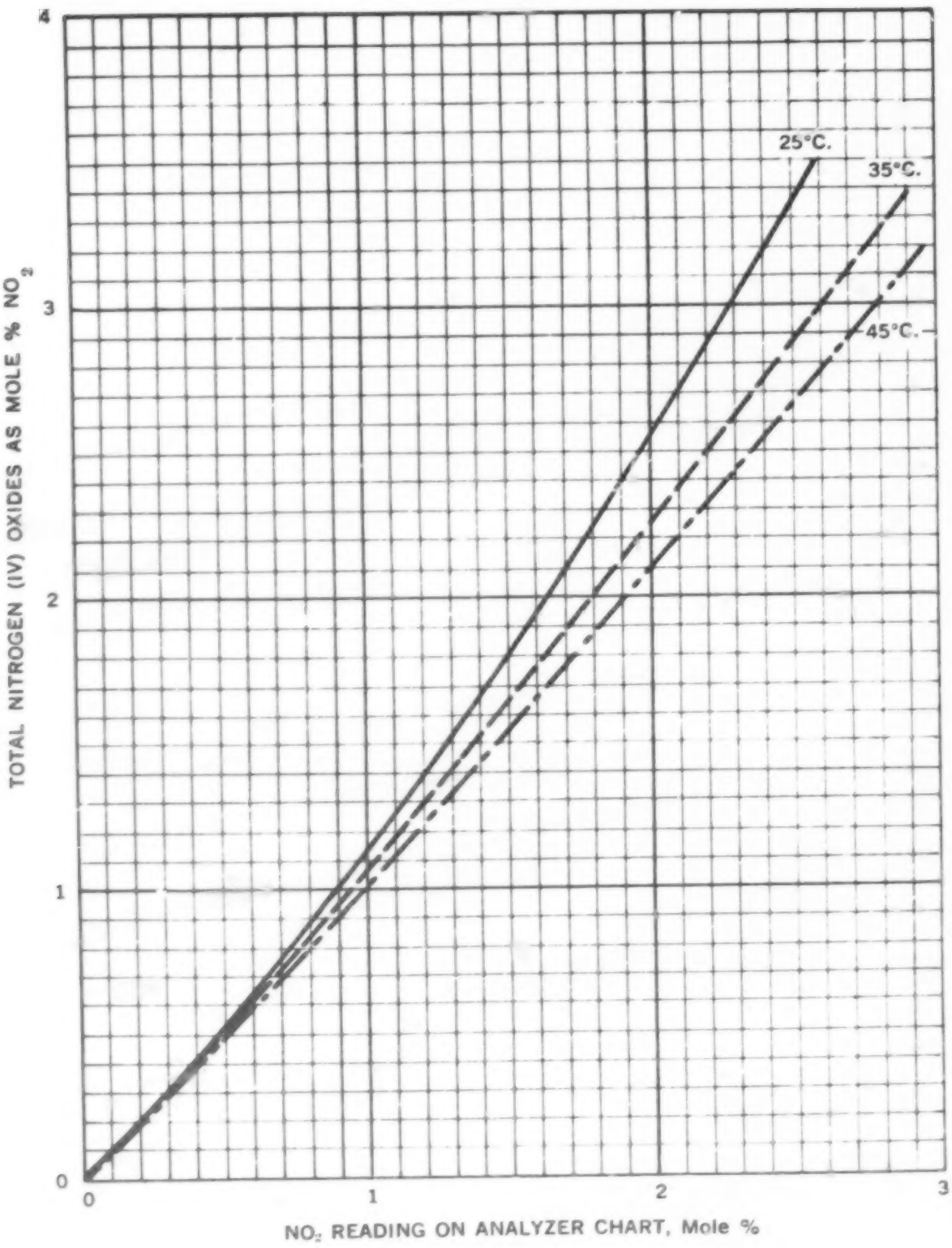


Figure A5 — Equilibrium data for 2 $NO_2 \rightleftarrows N_2O_4$.

## CALIBRATION OF THE MODEL 4 ANALYZER AND SECONDARY STANDARD GLASS FILTERS

For an accurate check of analyzer performance, calibrate the analyzer by chemically analyzing a set of samples of different concentrations collected at the analyzer outlet.

Zero the analyzer.

Set the SPAN control so the calibration gas containing the highest concentration of $NO_2$ drives the recorder nearly to full scale.

Flush the cell with purge gas immediately before collecting each sample in order to check the instrument zero.

Pass the $NO_2 - N_2$ standard mixture from the gas cylinder through the cell, adjusting the flow rate to not less than 500 ml/min for a 10 cm cell. Collect a gas sample at the cell outlet in 300-to-500-ml gas-sampling bulb. Purge the sampling bulb for 5 minutes with the gas sample. Note the recorder deflection and record the designation of the corresponding sample during the sample collection.

Determine total nitrogen (IV) oxides in the gas samples as described in the $H_2O_2$ method.

After collecting the last sample, re-zero the analyzer and, without changing the SPAN setting, insert the calibration filter and note the deflection on the recorder.

Plot recorder readings versus mole percent $NO_2$ as in Figure A6. Mole percent $NO_2$ is obtained by converting the total nitrogen (IV) oxides value obtained by the modified Gaillard procedure to mole percent $NO_2$ by use of the equilibrium data plotted in Figure A5. The plot of recorder readings versus mole percent $NO_2$ (Figure A6) is linear in the range from 0 to 2 percent $NO_2$.

From the curve plotted, determine what mole percent $NO_2$ is equivalent to the recorder deflection for the calibration filter. For example, a single 3-75 (3060) filter gives a recorder reading of 24.3 percent of full scale, which is equivalent to 0.24 mole percent $NO_2$ according to Figure A6.

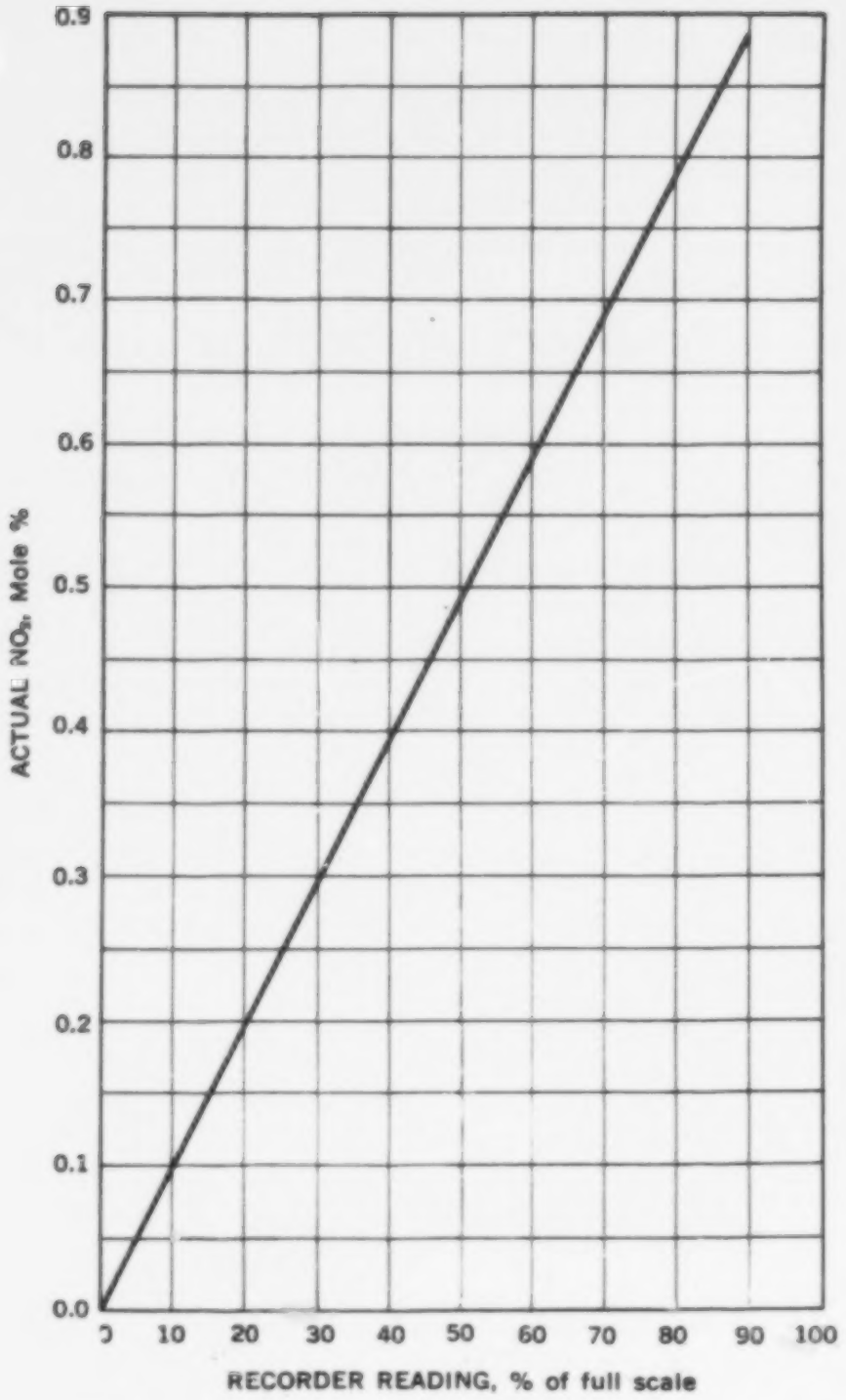


Figure A6 — Calibration curve for model 4 analyzer (10-cm cell; span, 136).

## DETERMINATION OF ACID MIST

### DESCRIPTION OF SAMPLING EQUIPMENT

The sampling equipment used for acid mist was constructed by the Public Health Service and is based on the equipment used by the Monsanto Company. This portable train allows collection of a wide range of mist or dust concentrations in a minimum of time. Particles greater than 3 microns diameter are determined separately from the smaller particles.

The Public Health Service sampling train, Figures A7 and A8, consists of a glass probe, a high-efficiency glass cyclone to collect particles larger than 3 microns diameter, and a filter that traps the smaller particles. A calibrated orifice, dry gas meter, and pump complete the train. This train was originally designed for the collection of sulfuric acid mist, but it serves equally well for nitric acid mist.

To prevent condensation of moisture in the train, the collection system is mounted in a heated, insulated box. Heating is accomplished by two thermostatically controlled electric heaters mounted in a transite box within the sampler. The heaters are rated at 1000 watts each at 110 volts. They consist of cone-shaped ceramic holders wound with heating wire and are commonly called bowl heaters. The transite box is open at each end, and a small fan circulates hot air around the collection equipment. Temperatures should be kept above the water dew point, but not above the acid dew point.

On the other side of the sampling box are mounted two manometers to indicate flow rate through the train, two dial stem thermometers to measure

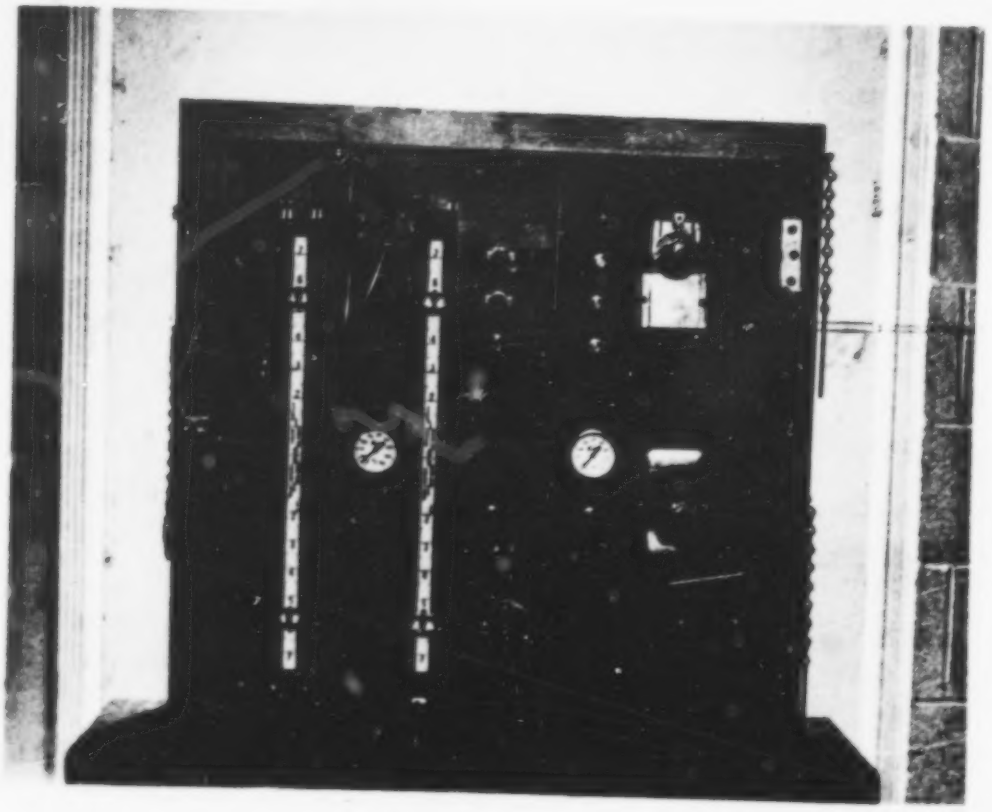

Figure A7 — Acid mist sampling train, control panel.

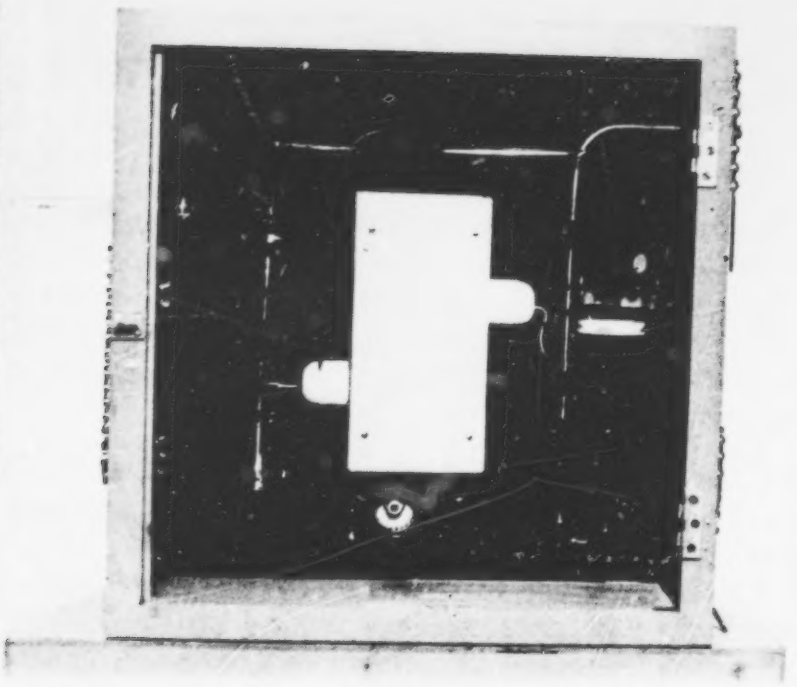

Figure A8 — Acid mist sampling train, collection compartment.

temperatures at the cyclone and orifice, and a temperature-controlling thermostat.

The filter consists of a 65-mm-diameter glass Buchner funnel with a course-porosity filtering disc. Two layers of fiberglass filter paper (MSA CT 75428) are placed on the filtering disc to form the acid mist filter. The packed fiberglass wool filter (Pyrex 3950) as described by Monsanto is also highly efficient. (*16*)

The dry gas meter may be omitted if the rate of flow through the calibrated orifice is carefully watched. In the field, however, circumstances may prevent careful observation of flow rate, and a dry gas meter insures accurate measurement of total volume flow.

## SELECTION OF SAMPLING POINTS

The location and number of sampling points are based on size and shape of the duct, uniformity of gas flow in the duct, availability of sampling port, and space required to set up sampling equipment.

Straight vertical ducts with no flow obstructions for at least 8 diameters upstream of the sampling point are preferred. Sometimes one must settle for less than these ideal conditions.

To insure a representative sample of stack gas, the duct should be divided into a number of equal areas and sampled at the center of each of these areas. The number of areas depends on the size of the stack. This procedure prevents erroneous results due to stratification of the acid mist in

the duct. Bulletin WP-50 of the Western Precipitation Company may prove useful in determining the number of areas.

## STACK GAS VELOCITY

The pitot tube is used for most velocity measurements. The basic equation for calculating velocity is,

$$V_s = 174K \sqrt{HT_s} \times \frac{29.9}{P_s} \times \frac{29.0}{MW}$$ where $V_s$ is the gas velocity in feet per minute, K is the pitot tube calibration factor, H is the velocity head in inches of water, $T_s$ is the stack gas temperature in °R, $P_s$ is the absolute pressure of stack gas in inches of mercury, and MW is the molecular weight of the process gas. This equation simplifies to $V_s = 174 \sqrt{HT_s}$ when the stack pressure is approximately equal to 29.9 and the molecular weight of the process gas is equal to that of air (29.0).

## SAMPLING RATE DETERMINATION

In the use of the acid mist train, a sampling rate of about 1 cfm at 70°F must be maintained in order to insure separation of particles larger than 3 microns diameter in the cyclone.

Nozzle area is then determined by dividing sampling rate by stack gas velocity, i.e.

$$A_n = \frac{\text{Q, sampling rate at stack gas conditions}}{\text{V}_s\text{, stack gas velocity}}$$

If the gas temperature is below the acid dew point at the sampling port, the mist must be sampled isokinetically.

It is, of course, impractical to vary nozzle size once sampling has begun. Therefore, if gas velocity varies considerably, the sampling rate must be varied and either cyclone efficiency or isokinetic sampling must be sacrificed. Isokinetic sampling is not necessary if previous testing has shown that about 90 percent of the acid mist particles are below 3 to 5 microns diameter.

Sampling rates and the corresponding orifice pressure drop should be computed for each sampling point before sampling is begun. These values should be recorded on the data sheet, Figure A9. Care must be taken in using the orifice calibration curve at various temperatures and pressures. A typical orifice calibration curve is shown in Figure A10. The following equations may prove useful:

$$\Delta P_o = \Delta P \text{ (calib)} \times \frac{530}{T_o} \times \frac{P_b - P_o}{29.9} \times \frac{MW}{29.0}$$

$$Q_o = Q \text{ (calib)} \times \frac{T_o}{530} \times \frac{29.9}{P_b - P_o}$$

$\Delta P_o$ = pressure drop across orifice at orifice pressure and temperature, in. $H_2O$

$P_b$ = barometric pressure, in. Hg

$\Delta P$ (calib) = pressure drop across orifice at orifice calibration conditions, in. $H_2O$

$T_o$ = temperature at orifice, °R

$P_o$ = gauge pressure at inlet to orifice, in. Hg.

MW = molecular weight of gas
$Q_o$ = flow through orifice at orifice temperature and pressure, cfm
Q (calib) = flow through orifice at calibration conditions, cfm

Plant _____ Date _____

Location _____ Test No. _____

$P_b$ = _____

| | | ORIFICE DATA* | | | | METER DATA | | |
|---|---|---|---|---|---|---|---|---|
| Position | Time, min | Desired flow, cfm $=A_n \times V_s$ | $\Delta P_o$, in. $H_2O$ | $T_o$, °F | $P_o$, in. Hg | Reading, $ft^3$ $Q_m$ | $P_m$, in. $H_g$ | $T_m$, °F |
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*At stack conditions.

$$\Delta P_o = \Delta P_{(Calib)} \left( \frac{530}{460+T_o} \times \frac{P_b - P_o}{29.9} \times \frac{MW}{29.0} \right) =$$

$$Q_s = \text{Volume sampled in scf} = Q_m \times \frac{530}{460 + T_m} \times \frac{P_b - P_m}{29.9} =$$

| | TITRATIONS cc of NaOH, N=___ | mg $HNO_3$ = cc x N x 63 | CONC. $mg/ft^3$ |
|---|---|---|---|
| CYCLONE | | | |
| FIBER FILTER | | | |
| TOTAL | | | |

Figure A9 — Data sheet for sampling nitric acid mist.

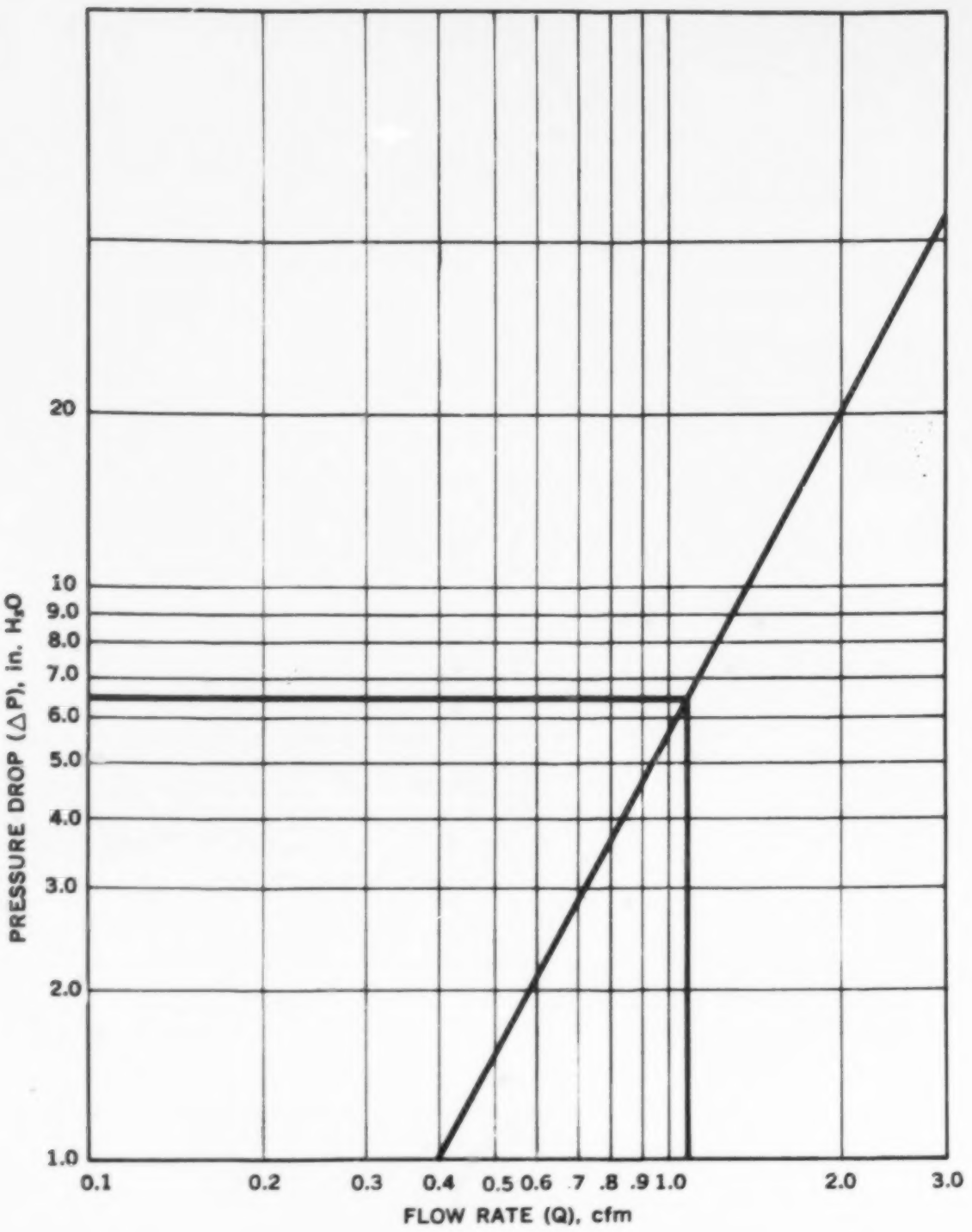


Figure A10 — Typical orifice calibration curve at 70°F and 29.9 in. Hg.

## A SAMPLE CALCULATION ILLUSTRATES THE PROCEDURE

Assume $T_o = 100°F$, $P_o = 2$ in. Hg, MW = 29.0, and $P_b = 29.9$ in. Hg. Desired sampling rate at 70°F is 1 ft³/min or 1.05 ft³/min at 100°F (the stack temperature). Stack velocity measured by pitot tube measurements was 1350 ft/min. The sample nozzle area is then equal to

$$\frac{1.05 \text{ ft}^3/\text{min}}{1350 \text{ ft/min}} = 0.778 \times 10^{-3} \text{ ft.}^2$$

The area of the probe selected was $0.8 \times 10^{-3}$ ft.².

The required flow at the sampling point is the stack velocity times the probe area or 1350 ft/min x 0.8 x $10^{-3}$ $ft^2$ = 1.08 $ft^3$/min at stack temperature and pressure.

The corresponding orifice pressure drop at this flow is obtained by (1) entering the orifice calibration chart at the desired gas volume and reading the orifice pressure drop and (2) converting this pressure drop to conditions under which the orifice will operate.

i.e. 1. Enter chart at 1.08 cfm and read $\Delta P$ = 6.5 in. at calibration conditions.

2. $\Delta P_o = 6.5 \text{ in.} \times \frac{530}{560} \times \frac{29.9\text{-}2.0}{29.9} \times \frac{29.0}{29.0} = 5.74 \text{ in.}$

at orifice conditions.

Desired orifice setting is then 5.74 in. at this sampling point.

## SAMPLE COLLECTION

Place two thicknesses of fiberglass filter paper in the glass filter holder or firmly pack filter tube with glass wool to a depth of 2 inches, depending on which type of filtering system is used. Check the packing by drawing air through the train at about 1 cfm. A pressure drop of about 3 in. Hg indicates sufficient fiber wool packing.

Pressure check the train by plugging the probe and drawing a vacuum of 6 in. Hg. Close the line leading from the train; the vacuum should remain at 6 in. Hg if the train is leakproof. *Slowly* remove plug from probe to release vacuum and open line leading from train.

Close insulated door on sampling train and heat collection apparatus to 10°F above stack temperature. *Blower should be* ON whenever box is hot. Regulate temperature with the thermostat on front of box.

Insulate probe to prevent condensation during cold weather.

When sample box reaches operating temperature, sampling can begin. During testing, record all pertinent data on the data sheet. Compute the desired flow and the corresponding pressure drop before sampling begins.

Normally a sample collection period of 20 to 30 minutes at a sampling rate of approximately 1 cfm should be sufficient. If expected acid mist loadings are high, i.e. 50 mg per scf, it is possible to overload the glass filter media regardless of which type is used. In any case, the glass tubing downstream of the filter should be inspected often. Any carryover of acid mist will be indicated by droplets or liquid in the tubing.

## SAMPLE ANALYSIS

When sampling is completed, allow train to cool. Remove collected sample from probe and cyclone by rinsing with distilled water and collecting

washings in a 500-ml beaker. Add five drops of phenolphthalein indicator solution and titrate with a standardized NaOH solution. For lower acid mist loadings of 0.5 to 50 mg/scf, use an NaOH solution of about 0.01 to 0.1N. For higher loadings, use a normality of about 1.0.

Remove the filter paper or glass wool from its holder and place in a beaker. Rinse the cyclone outlet line and the glass filter holder with distilled water and add this washing to the beaker with the filter. Add enough distilled water to thoroughly remove all of the acid mist from the filter and form a slurry. Stir the solution of paper or glass wool and water vigorously for 15 to 20 minutes to insure a uniform mixture. Vigorous stirring should also be employed during the titration with NaOH solution to determine an accurate end point. When glass wool is used as a filtering medium, a stainless steel stirring rod is recommended for stirring the rather thick fluffy mixture of glass wool and water; many glass rods have been broken.

Since there are 63 mg $HNO_3$ per cc of 1.0 NaOH solution, (cc NaOH) (N NaOH) (63) = mg $HNO_3$.

Take duplicate samples. Run blank titration on whichever filter medium is used because some NaOH may be needed to neutralize the medium.

## APPENDIX B: NITRIC ACID ESTABLISHMENTS IN THE UNITED STATES

The following tabulation was compiled largely on the basis of a questionnaire sent to all known nitric acid producers in September 1964, updated with additional information obtained from the literature and by personal contact with company representatives. The list indicates only the establishment at a given location and not the number of individual producing units.

The "process" column relates to the operating pressures:

A—Atmospheric: Oxidation of ammonia and absorption at atmospheric pressure (10 psig maximum).

I—Intermediate: Oxidation of ammonia and absorption at an intermediate pressure of 20 to 60 psig.

P—Pressure: Oxidation of ammonia and absorption of the resulting nitrogen oxides at pressures of 80 to 120 psig.

## U. S. NITRIC ACID ESTABLISHMENTS

January 1966

| Company | Location | Process | Nominal[a] Capacity, short tons of 100% $HNO_3$ per year |
|---|---|---|---|
| *ALABAMA* | | | |
| Armour Agricultural Chemical Company | Cherokee | P | 105,000 |
| E. I. du Pont de Nemours & Company | Mineral Springs | P | 20,000 |
| Hercules Powder Company, Inc. | Bessemer | P | 15,000 |
| Ketona Chemical Corporation | Ketona | P | 23,000 |
| Tennessee Valley Authority | Wilson Dam | P | 100,000 |
| *ARIZONA* | | | |
| Apache Powder Company | Curtiss | P | 35,000 |
| *ARKANSAS* | | | |
| Monsanto Company | El Dorado | P | 255,000 |
| *CALIFORNIA* | | | |
| Collier Carbon and Chemical Corporation | Brea | P | 47,000 |
| Hercules Powder Company, Inc. | Hercules | P | 100,000 |
| Ortho Div., Chevron Chemical Company | Richmond | P | 80,000 |
| Shell Chemical Company | Ventura | P | 20,000 |
| *COLORADO* | | | |
| E. I. du Pont de Nemours & Company | Louviers | P | 20,000 |
| *FLORIDA* | | | |
| Chemstrand Company, a div. of Monsanto Company | Pensacola | P | 220,000 |
| Escambia Chemical Corporation | Pensacola | P | 85,000 |
| Southern Nitrogen Company, Inc. | Tampa | P | 42,000 |
| *GEORGIA* | | | |
| Columbia Nitrogen Corporation | Augusta | I | 145,000 |
| Southern Nitrogen Company, Inc. | Bainbridge | P | 43,000 |
| Southern Nitrogen Company, Inc. | Savannah | P | 142,000 |

[a] Rounded to nearest 500 net tons

[b] Unconfirmed

| Company | Location | Process | Nominal* Capacity, short tons of 100% $HNO_3$ per year |
|---|---|---|---|
| *ILLINOIS* | | | |
| Commercial Solvents Corp. | Ordill | P | 50,000 |
| E. I. du Pont de Nemours & Company | Seneca | P | 40,000 |
| Illinois Nitrogen Corporation | Marseilles | P | 115,500 |
| Nitrin, Inc. | Cordova | P | 85,000 |
| Texaco Inc. | Lockport | P | 66,000 |
| U. S. Industrial Chemicals Co., Div. of *National Distillers and Chemical* Corporation | Tuscola | P | 40,000 |
| *INDIANA* | | | |
| Calumet Nitrogen Products Company | Hammond | P | 39,500 |
| Central Nitrogen, Inc. | Terre Haute | P | 122,500 |
| *IOWA* | | | |
| Hawkeye Chemical Company | Clinton | P | 117,000 |
| Ortho Div., Chevron Chemical Company | Fort Madison | P | 80,000 |
| *KANSAS* | | | |
| Cooperative Farm Chemicals Association | Lawrence | P | 220,000 |
| Spencer Chemical Div.— | Pittsburg | P | 140,000 |
| Gulf Oil Corporation | | I | 140,000 |
| *KENTUCKY* | | | |
| Spencer Chemical Div.— Gulf Oil Corporation | Henderson | P | 80,000 |
| *LOUISIANA* | | | |
| Commercial Solvents Corporation | Sterlington | P | 158,500 |
| Monsanto Company | Luling | P | 218,000 |
| Olin Mathieson Chemical Corporation | Lake Charles | P | 93,000 |
| Rubicon (U. S. Rubber—ICI) | Geismar | P | 25,000 |
| *MAINE* | | | |
| Northern Chemical Industries, Inc. | Searsport | P | 20,000 |
| *MINNESOTA* | | | |
| St. Paul Ammonia Products, Inc. | Pine Bend | P | 70,000 |
| *MISSISSIPPI* | | | |
| Mississippi Chemical Corporation | Yazoo City | P | 260,000 |
| Spencer Chemical Div.— Gulf Oil Corporation | Vicksburg | P | 80,000 |

| Company | Location | Process | Nominal[a] Capacity, short tons of 100% $HNO_3$ per year |
|---|---|---|---|
| *MISSOURI* | | | |
| Armour Agricultural Chemical Company | Crystal City | P | 100,000 |
| Atlas Chemical Industries, Inc. | Webb City | P | 91,500 |
| Hercules Powder Company, Inc. | Louisiana | P | 350,000 |
| *NEBRASKA* | | | |
| Allied Chemical Corporation, Nitrogen Div. | La Platte | P | 93,500 |
| Feltex, Inc. | Fremont | P | 30,000 |
| Cominco Products | Beatrice | P | 125,000 |
| *NEW JERSEY* | | | |
| American Cyanamid Company | Bound Brook | I | 21,500 |
| E. I. du Pont de Nemours & Company | Gibbstown | P | 220,000 |
| Hercules Powder Company, Inc. | Kenvil | P | 15,000 |
| Hercules Powder Company, Inc. | Parlin | P | 40,000 |
| *NEW YORK* | | | |
| Allied Chemical Corporation, Nitrogen Div. | Buffalo | A | 25,000 |
| M. Ames Chemical Works, Inc. | Glens Falls | I | 500 |
| *NORTH CAROLINA* | | | |
| Carolina Nitrogen Corporation | Wilmington | P | 130,000 |
| *OHIO* | | | |
| Allied Chemical Corporation, Nitrogen Div. | South Point | A | 239,000 |
| Solar Nitrogen Chemical Co. | Lima | P | 65,000 |
| Southern Nitrogen Company, Inc. | Cincinnati | P | 76,000 |
| *PENNSYLVANIA* | | | |
| Allied Chemical Corporation, General Chemical Div. | Newell | P | 65,000 |
| Atlas Chemical Industries, Inc. | Reynolds | P | 17,500 |
| *TENNESSEE* | | | |
| E. I. du Pont de Nemours & Company | Old Hickory | P | 42,000 |
| Farmers Chemical Association | Chattanooga | P | 125,000[b] |

| Company | Location | Process | Nominal[a] Capacity, short tons of 100% $HNO_3$ per year |
|---|---|---|---|
| *TEXAS* | | | |
| Celanese Chemical Company | Bay City | P | 30,000 |
| E. I. du Pont de Nemours & Company | Beaumont | P | 60,000 |
| E. I. du Pont de Nemours & Company | Orange | P | 85,000 |
| Nipak, Inc. | Kerens | P | 49,000 |
| Phillips Petroleum Company | Etter | P | 157,500 |
| El Paso Natural Gas | Odessa | P | 65,000 |
| *UTAH* | | | |
| United States Steel Corporation | Provo | I | 59,500 |
| *VIRGINIA* | | | |
| Allied Chemical Corporation, Nitrogen Div. | Hopewell | P | 380,000 |
| Hercules Powder Company, Inc. | Radford | P | 100,000 |
| *WASHINGTON* | | | |
| E. I. du Pont de Nemours & Company | Du Pont | P | 20,000 |
| Ortho Div., Chevron Chemical Company | Kennewick | P | 50,000 |
| Phillips Pacific Chemical Company | Kennewick | P | 7,000 |
| *WEST VIRGINIA* | | | |
| American Cyanamid Company | Willow Island | P | 24,000 |
| E. I. du Pont de Nemours & Company | Belle | P | 85,000 |
| *WISCONSIN* | | | |
| E. I. du Pont de Nemours & Company | Barksdale | P | 20,000 |

| | Tons $HNO_3$ per year |
|---|---|
| Pressure Process | 6,190,000 |
| Intermediate | 366,500 |
| Atmospheric | 264,000 |
| TOTAL | 6,820,500 |

Number of Establishments — 74

# APPENDIX C: FACTORS CAUSING HIGH EMISSIONS OF NITROGEN OXIDES

A number of factors, alone or in combination, can cause abnormally high emissions of nitrogen oxides in the stack gases that are discharged to the atmosphere. The causes and methods of control are tabulated on the following pages.

## PRESSURE AND COMBINATION PROCESSES

### LEAKING HEAT EXCHANGERS

Cold exit gas from the absorption tower is generally reheated by heat exchange with hot rich converter gas, before it passes to a power recovery turbine and on to the atmosphere. A faulty heat exchanger allows rich gas to leak into the exit gas stream, resulting in excessive nitrogen oxides concentration in the tail gas. Analysis of the exit gas for nitrogen oxides content as it enters and as it leaves the reheater will show whether leakage is occurring.

### INSUFFICIENT OXYGEN SUPPLY TO PROCESS

Enough air must be supplied to the process to provide the oxygen needed for oxidation of ammonia and for the subsequent reactions of nitrogen oxides to form nitric acid. Under proper operating conditions there should be a small excess of unreacted oxygen in the exit gas leaving the absorber, usually about 3 or 4 percent. A deficiency of oxygen will result in incomplete reaction and consequently in excess nitrogen oxides in the stack gas. Proper control of air and ammonia flows can correct this situation.

### COOLING WATER—INSUFFICIENT FLOW OR HIGH TEMPERATURE

Good cooling of the condensers and the absorption column is essential for maximum absorption efficiency. An ample flow of cooling water is mandatory. Best performance is obtained with cold water. In warm weather the cooling water supply may reach temperatures of 90°F or more, with a consequent decrease in absorption efficiency and increase in tail gas emission. The solution to the problem is to provide better cooling or to install facilities for fume elimination.

### PRODUCTION RATE AND ACID STRENGTH

Nitric acid plants can be operated above rated capacity by increasing the flows of air and ammonia. The acid strength can also be increased beyond design (usually 55 to 60 percent $HNO_3$) by a few percent. Both of these actions lead to a sacrifice in yield and an increase in tail-gas emission. Under these circumstances, fume elimination facilities may be required.

### EQUIPMENT FAILURES

Performance of the absorption column can be adversely affected by failure of the internal parts as a result of corrosion or mechanical breakdown. Usually this failure can be detected by determining the acid strength gradient throughout the column.

Chlorides can cause severe corrosion of stainless steel; it is customary to sample the nitric acid at an intermediate point in the absorber (where the acid strength is about 23 percent $HNO_3$), and determine its chloride content. If the chloride content exceeds 0.03 to 0.05 percent, the 23 percent nitric acid should be drained from the absorber tray; otherwise, a further accumulation of chlorides would lead to serious corrosion.

### PROCESS FEED WATER

Distilled water (steam condensate) is fed to the top of the absorber and takes part in the reaction with nitrogen oxides to form nitric acid. Failure to supply the required quantity of process water to the absorber will result in excessive emission of nitrogen oxides in the tail gas.

## ATMOSPHERIC PROCESS

Emission problems in the atmospheric process are essentially the same as those encountered in the pressure process. The two processes differ substantially, however, in the design of absorption systems. Whereas the pressure process utilizes a single-pass bubble-cap absorber with internal cooling, the atmospheric plant comprises a series of packed towers over each of which acid is circulated by pumps. Generally, the circulating acid flows through coolers.

Difficulties that could lead to excessive emission of nitrogen oxides in an atmospheric plant absorption system are:

*Failure of one or more of the acid circulating pumps* to circulate sufficient acid.

*Poor acid distribution* in the top of the absorbers.

*Channeling* due to dirty tower.

*Inadequate cooling* of the circulating acid, caused by dirty coolers or insufficient water flow.

# APPENDIX D
# PHYSICAL DATA

## PHYSICAL DATA — NITRIC ACID(*17*)

| Be.° | Sp. Gr. | Tw.° | % $HNO_3$ |
|---|---|---|---|
| 10.00 | 1.0741 | 14.82 | 12.86 |
| 10.25 | 1.0761 | 15.22 | 13.18 |
| 10.50 | 1.0781 | 15.62 | 13.49 |
| 10.75 | 1.0801 | 16.02 | 13.81 |
| 11.00 | 1.0821 | 16.42 | 14.13 |
| 11.25 | 1.0841 | 16.82 | 14.44 |
| 11.50 | 1.0861 | 17.22 | 14.76 |
| 11.75 | 10.881 | 17.62 | 15.07 |
| 12.00 | 1.0902 | 18.04 | 15.41 |
| 12.25 | 1.0922 | 18.44 | 15.72 |
| 12.50 | 1.0943 | 18.86 | 16.05 |
| 12.75 | 1.0964 | 19.28 | 16.39 |
| 13.00 | 1.0985 | 19.70 | 16.72 |
| 13.25 | 1.1006 | 20.12 | 17.05 |
| 13.50 | 1.1027 | 20.54 | 17.38 |
| 13.75 | 1.1048 | 20.96 | 17.71 |
| 14.00 | 1.1069 | 21.38 | 18.04 |
| 14.25 | 1.109 | 21.80 | 18.37 |
| 14.50 | 1.11 | 22.22 | 18.70 |
| 14.75 | 1.1132 | 22.64 | 19.02 |
| 15.00 | 1.1154 | 23.08 | 19.36 |
| 15.25 | 1.1176 | 23.52 | 19.70 |
| 15.50 | 1.1197 | 23.94 | 20.02 |
| 15.75 | 1.1219 | 24.38 | 20.36 |
| 16.00 | 1.1240 | 24.80 | 20.69 |
| 16.25 | 1.1262 | 25.24 | 21.03 |
| 16.50 | 1.1284 | 25.68 | 21.36 |
| 16.75 | 1.1306 | 26.12 | 21.70 |
| 17.00 | 1.1328 | 26.56 | 22.04 |
| 17.25 | 1.1350 | 27.00 | 22.38 |
| 17.50 | 1.1373 | 27.46 | 22.74 |
| 17.75 | 1.1395 | 27.90 | 23.08 |
| 18.00 | 1.1417 | 28.34 | 23.42 |
| 18.25 | 1.1440 | 28.80 | 23.77 |
| 18.50 | 1.1462 | 29.24 | 24.11 |
| 18.75 | 1.1485 | 29.70 | 24.47 |
| 19.00 | 1.1508 | 30.16 | 24.82 |
| 19.25 | 1.1531 | 30.62 | 25.18 |
| 19.50 | 1.1554 | 31.08 | 25.53 |
| 19.75 | 1.1577 | 31.54 | 25.88 |
| 20.00 | 1.1600 | 32.00 | 26.24 |
| 20.25 | 1.1624 | 32.48 | 26.61 |
| 20.50 | 1.1647 | 32.94 | 26.96 |
| 20.75 | 1.1671 | 33.42 | 27.33 |
| 21.00 | 1.1694 | 33.88 | 27.67 |
| 21.25 | 1.1718 | 34.36 | 28.02 |
| 21.50 | 1.1741 | 34.82 | 28.36 |
| 21.75 | 1.1765 | 35.30 | 28.72 |
| 22.00 | 1.1789 | 35.78 | 29.07 |
| 22.25 | 1.1813 | 36.26 | 29.43 |
| 22.50 | 1.1837 | 36.74 | 29.78 |
| 22.75 | 1.1861 | 37.22 | 30.14 |
| 23.00 | 1.1885 | 37.70 | 30.49 |
| 23.25 | 1.1910 | 38.20 | 30.86 |
| 23.50 | 1.1934 | 38.68 | 31.21 |
| 23.75 | 1.1959 | 39.18 | 31.58 |
| 24.00 | 1.1983 | 39.66 | 31.94 |
| 24.25 | 1.2008 | 40.16 | 32.31 |
| 24.50 | 1.2033 | 40.66 | 32.68 |
| 24.75 | 1.2058 | 41.16 | 33.05 |
| 25.00 | 1.2083 | 41.66 | 33.42 |
| 25.25 | 1.2109 | 42.18 | 33.80 |
| 25.50 | 1.2134 | 42.68 | 34.17 |
| 25.75 | 1.2160 | 43.20 | 34.56 |
| 26.00 | 1.2185 | 43.70 | 34.94 |
| 26.25 | 1.2211 | 44.22 | 35.33 |
| 26.50 | 1.2236 | 44.72 | 35.70 |
| 26.75 | 1.2262 | 45.24 | 36.09 |
| 27.00 | 1.2288 | 45.76 | 36.48 |
| 27.25 | 1.2314 | 46.28 | 36.87 |
| 27.50 | 1.2340 | 46.80 | 37.26 |
| 27.75 | 1.2367 | 47.34 | 37.67 |
| 28.00 | 1.2393 | 47.86 | 38.06 |
| 28.25 | 1.2420 | 48.40 | 38.46 |
| 28.50 | 1.2446 | 48.92 | 38.85 |
| 28.75 | 1.2473 | 49.46 | 39.25 |
| 29.00 | 1.2500 | 50.00 | 39.66 |
| 29.25 | 1.2527 | 50.54 | 40.06 |
| 29.50 | 1.2554 | 51.08 | 40.47 |
| 29.75 | 1.2582 | 51.64 | 40.89 |
| 30.00 | 1.2609 | 52.18 | 41.30 |
| 30.25 | 1.2637 | 52.74 | 41.72 |
| 30.50 | 1.2664 | 53.28 | 42.14 |
| 30.75 | 1.2692 | 53.84 | 42.58 |
| 31.00 | 1.2719 | 54.38 | 43.00 |
| 31.25 | 1.2747 | 54.94 | 43.44 |
| 31.50 | 1.2775 | 55.50 | 43.89 |
| 31.75 | 1.2804 | 56.08 | 44.34 |

| Be.° | Sp. Gr. | Tw.° | % $HNO_3$. | Be.° | Sp. Gr. | Tw.° | % $HNO_3$. |
|---|---|---|---|---|---|---|---|
| 32.00 | 1.2832 | 56.64 | 44.78 | 40.50 | 1.3876 | 77.52 | 62.77 |
| 32.25 | 1.2861 | 57.22 | 45.24 | 40.75 | 1.3909 | 78.18 | 63.48 |
| 32.50 | 1.2889 | 57.78 | 45.68 | 41.00 | 1.3942 | 78.84 | 64.20 |
| 32.75 | 1.2918 | 58.36 | 46.14 | 41.25 | 1.3976 | 79.52 | 64.93 |
| 33.00 | 1.2946 | 58.92 | 46.58 | 41.50 | 1.4010 | 80.20 | 65.67 |
| 33.25 | 1.2975 | 59.50 | 47.04 | 41.75 | 1.4044 | 80.88 | 66.42 |
| 33.50 | 1.3004 | 60.08 | 47.49 | 42.00 | 1.4078 | 81.56 | 67.18 |
| 33.75 | 1.3034 | 60.68 | 47.95 | 42.25 | 1.4112 | 82.24 | 67.95 |
| 34.00 | 1.3063 | 61.26 | 48.42 | 42.50 | 1.4146 | 82.92 | 68.73 |
| 34.25 | 1.3093 | 61.86 | 48.90 | 42.75 | 1.4181 | 83.62 | 69.52 |
| 34.50 | 1.3122 | 62.44 | 49.35 | 43.00 | 1.4216 | 84.32 | 70.33 |
| 34.75 | 1.3152 | 63.04 | 49.83 | 43.25 | 1.4251 | 85.02 | 71.15 |
| 35.00 | 1.3182 | 63.64 | 50.32 | 43.50 | 1.4286 | 85.72 | 71.98 |
| 35.25 | 1.3212 | 64.24 | 50.81 | 43.75 | 1.4321 | 86.42 | 72.82 |
| 35.50 | 1.3242 | 64.84 | 51.30 | 44.00 | 1.4356 | 87.12 | 73.67 |
| 35.75 | 1.3273 | 65.46 | 51.80 | 44.25 | 1.4392 | 87.84 | 74.53 |
| 36.00 | 1.3303 | 66.06 | 52.30 | 44.50 | 1.4428 | 88.56 | 75.40 |
| 36.25 | 1.3334 | 66.68 | 52.81 | 44.75 | 1.4464 | 89.28 | 76.28 |
| 36.50 | 1.3364 | 67.28 | 53.32 | 45.00 | 1.4500 | 90.00 | 77.17 |
| 36.75 | 1.3395 | 67.90 | 53.84 | 45.25 | 1.4536 | 90.72 | 78.07 |
| 37.00 | 1.3426 | 68.52 | 54.36 | 45.50 | 1.4573 | 91.46 | 79.03 |
| 37.25 | 1.3457 | 69.14 | 54.89 | 45.75 | 1.4610 | 92.20 | 80.04 |
| 37.50 | 1.3488 | 69.76 | 55.43 | 46.00 | 1.4646 | 92.92 | 81.08 |
| 37.75 | 1.3520 | 70.40 | 55.97 | 46.25 | 1.4684 | 93.68 | 82.18 |
| 38.00 | 1.3551 | 71.02 | 56.52 | 46.50 | 1.4721 | 94.42 | 83.33 |
| 38.25 | 1.3583 | 71.66 | 57.08 | 46.75 | 1.4758 | 95.16 | 84.48 |
| 38.50 | 1.3615 | 72.30 | 57.65 | 47.00 | 1.4796 | 95.92 | 85.70 |
| 38.75 | 1.3647 | 72.94 | 58.23 | 47.25 | 1.4834 | 96.68 | 86.98 |
| 39.00 | 1.3679 | 73.58 | 58.82 | 47.50 | 1.4872 | 97.44 | 88.32 |
| 39.25 | 1.3712 | 74.24 | 59.43 | 47.75 | 1.4910 | 98.20 | 89.76 |
| 39.50 | 1.3744 | 74.88 | 60.06 | 48.00 | 1.4948 | 98.96 | 91.35 |
| 39.75 | 1.3777 | 75.54 | 60.71 | 48.25 | 1.4987 | 99.74 | 93.13 |
| 40.00 | 1.3810 | 76.20 | 61.38 | 48.50 | 1.5026 | 100.52 | 95.11 |
| 40.25 | 1.3843 | 76.86 | 62.07 | | | | |

Specific gravity determinations were made at 60°F, compared with water at 60°F.

From the specific gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = 145 - \left(\frac{145}{\text{sp. gr.}}\right)$$

Baumé hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

## ALLOWANCE FOR TEMPERATURE

At 10° — 20° Be. — 1/30° Be. or .00029 sp. gr. = 1°F.
20° — 30° Be. — 1/23° Be. or .00044 sp. gr. = 1°F.
30° — 40° Be. — 1/20° Be. or .00060 sp. gr. = 1°F.
40° — 48.5° Be. — 1/17° Be. or .00084 sp. gr. = 1°F.

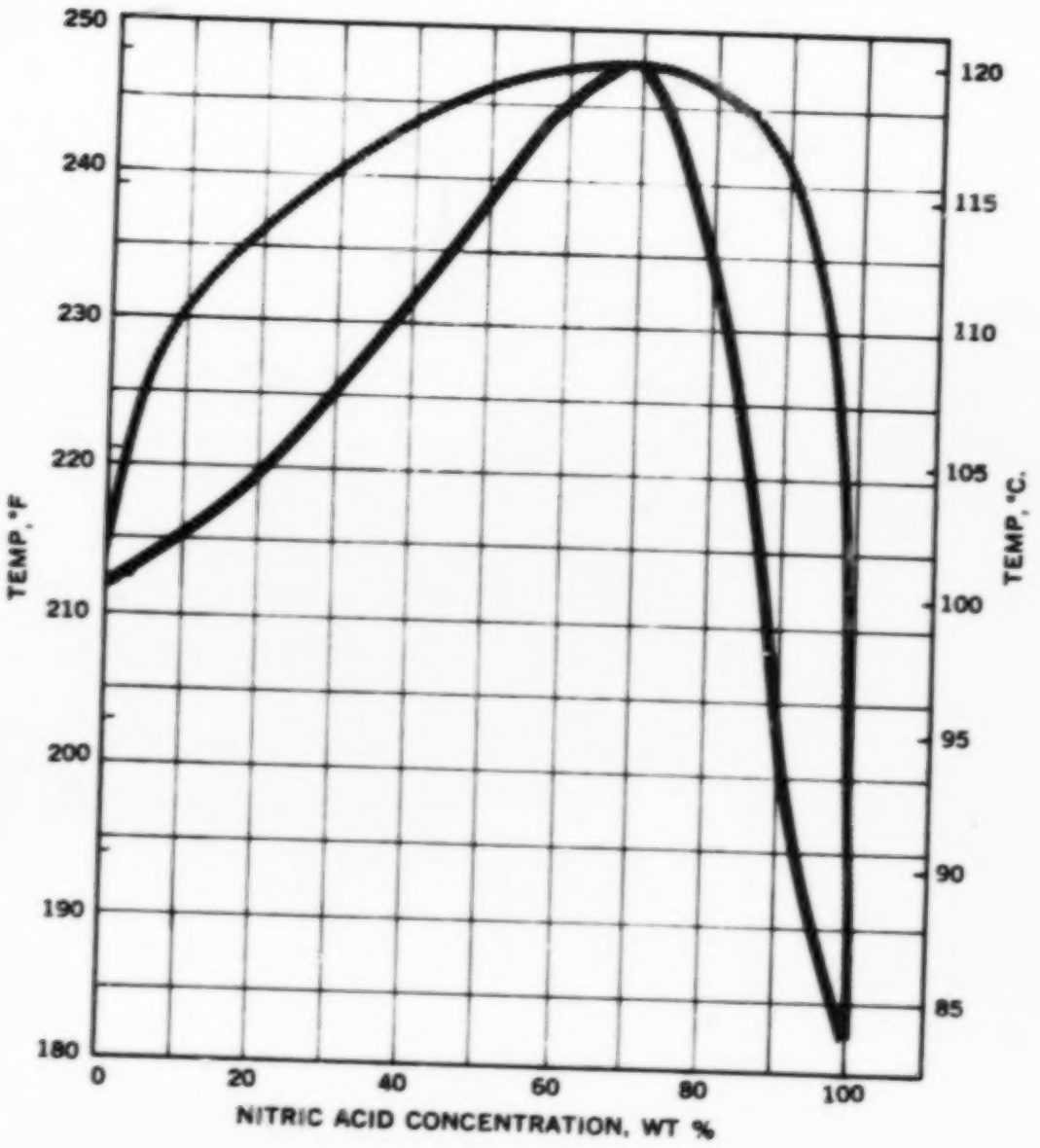


Figure D1 — Boiling point and vapor equilibrium diagram for nitric acid/water solutions of atmospheric pressure(*18*).

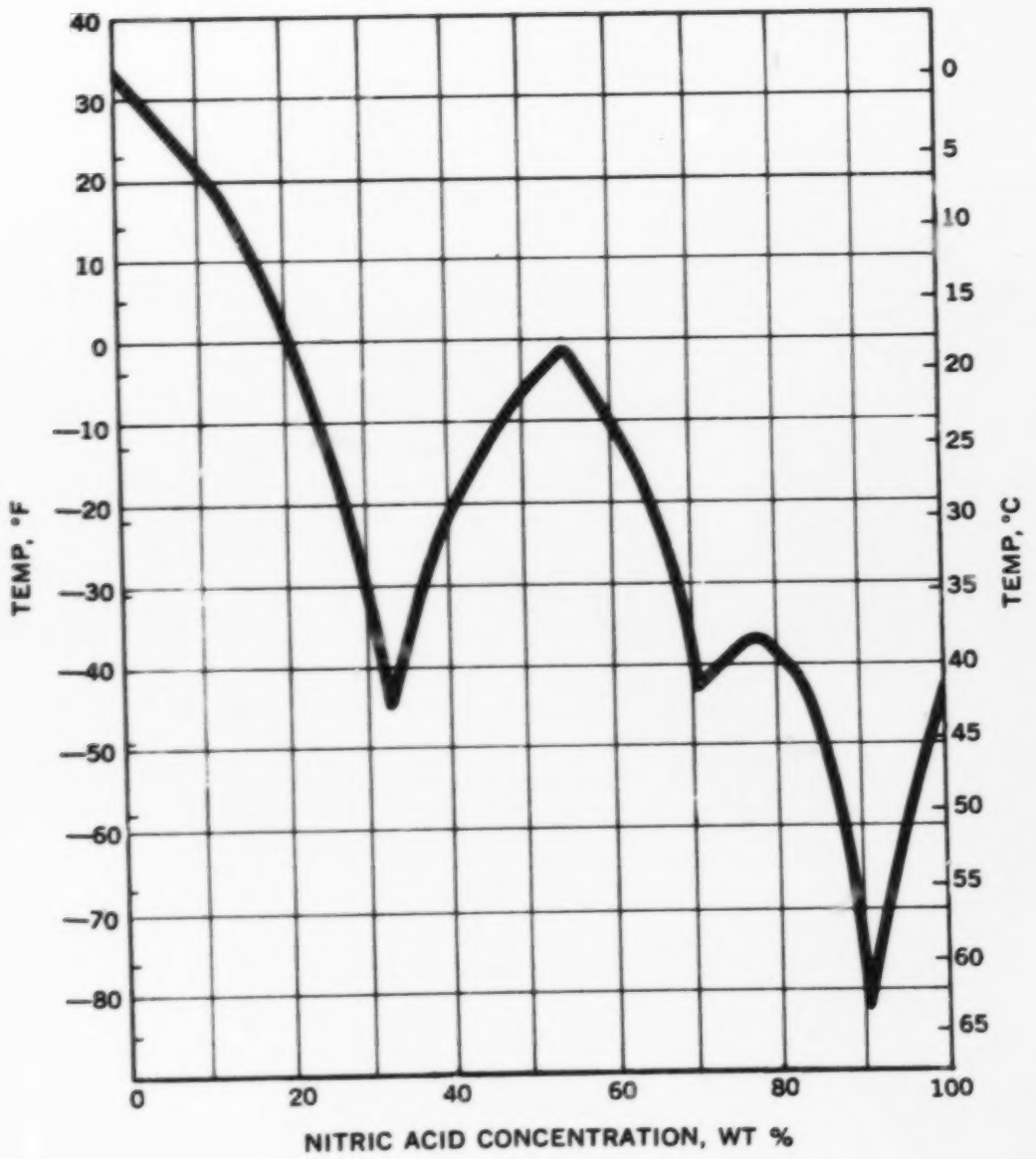


Figure D2 — Effect of concentration on normal freezing points of nitric acid/water solutions(*19*).

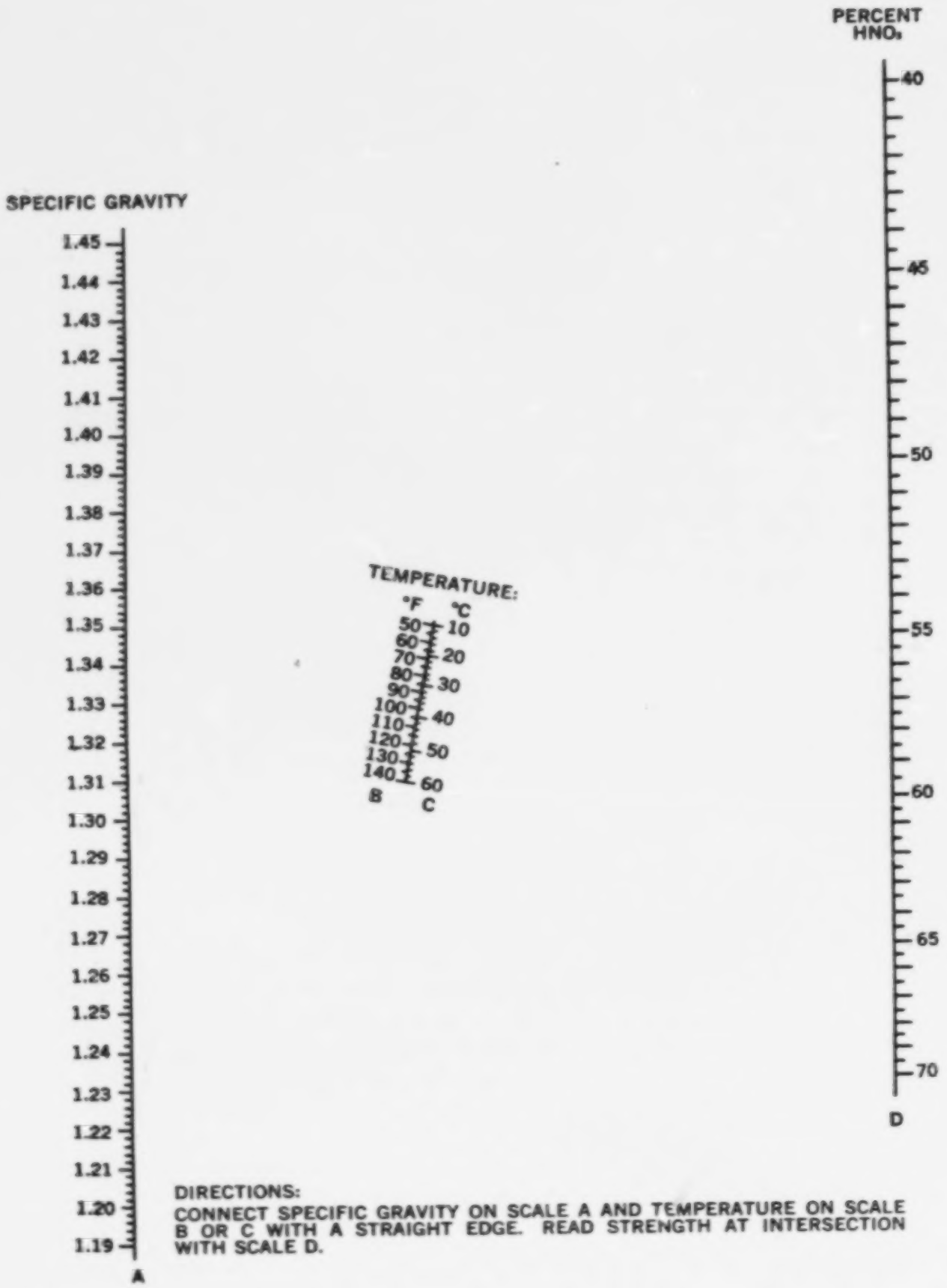


Figure D3 — Nomograph relating specific gravity and acid strength for weak nitric acid.

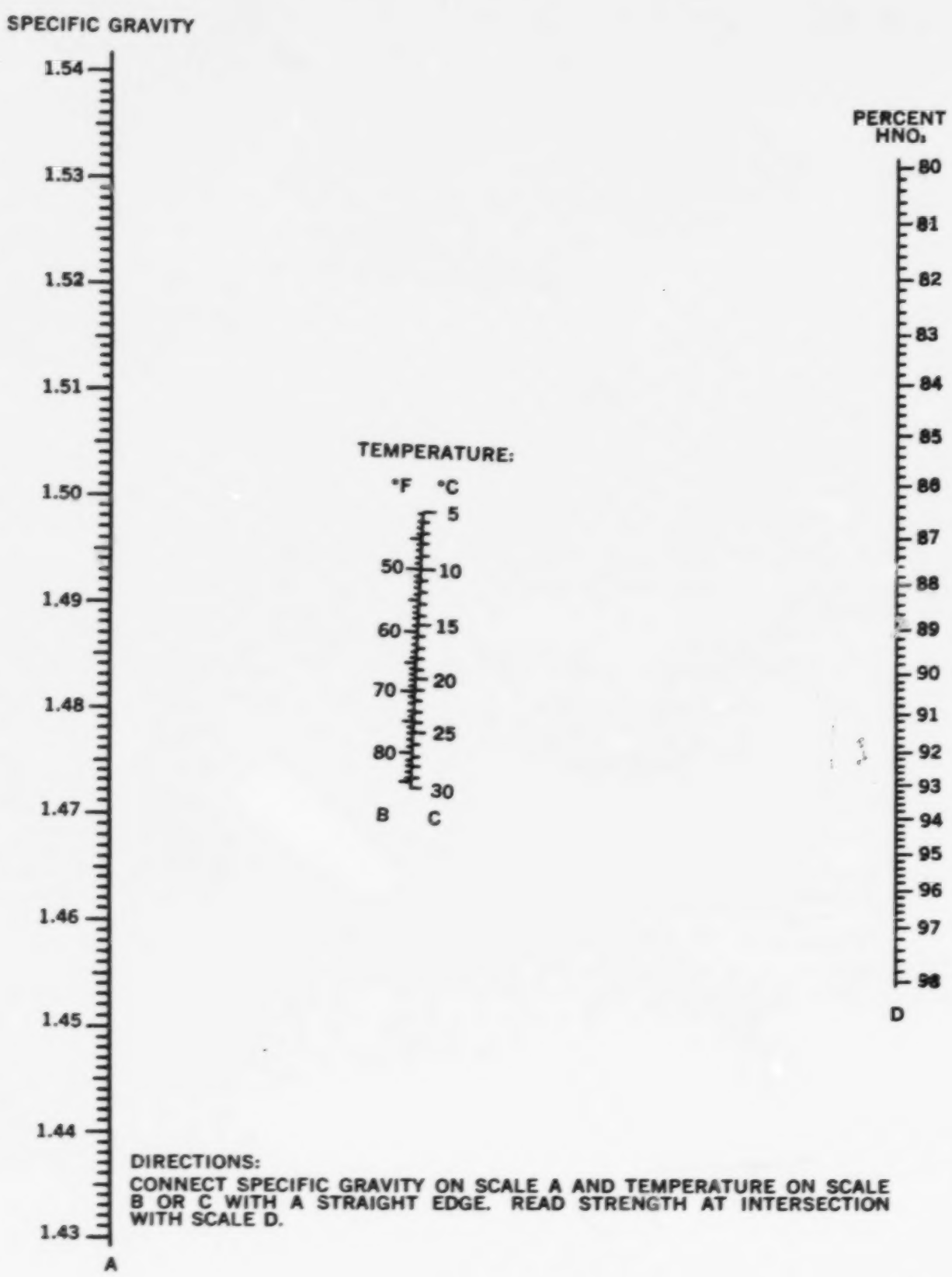


Figure D4 — Nomograph relating specific gravity and acid strength for strong nitric acid.

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